# INSTITUTE NOTES.

MARCH, 1941.

## FORTHCOMING MEETINGS.

Tuesday, 1st May, 1941, at 12.45 for 1 p.m., at the rooms of the Royal Empire Society, Northumberland Avenue, London, W.C.2 (by courtesy of the Council of the R.E.S.). **Institute Luncheon.** Further particulars will be circularized to members in Great Britain during April.

3 p.m. **Annual General Meeting** (to be held in the Lecture Hall of the Royal Empire Society).

3.30 p.m. (approx.) Address by the President, Prof. A. W. Nash, M.Sc., M.I.Mech.E.: **"Petroleum as a Raw Material."**

## NEW MEMBERS.

The following elections were made at a Council meeting held on 11th March, 1941.

Elections are subject to confirmation in accordance with the By-Laws, Section IV, paragraphs 9 and 10.

*As Fellows.*

OOSTON, William Hermanus ... ... ... ... ... England.

*Transfer to Fellows.*

MACKIE, William Frederick Charles ... ... ... ... England.

*As Members.*

PENARD, Herbert F. L. ... ... ... ... ... ... England.

*As Associate Members.*

CROOK, Roy Dallas ... ... ... ... ... ... ... S. Australia.
FORD, Alexander Langridge ... ... ... ... ... England.
WITHERS, George ... ... ... ... ... ... ... Transvaal.

*As Students.*

DRIVER, Anthony Victor ... ... ... ... ... ... England.
POOLE, Walter George ... ... ... ... ... ... England.

## CANDIDATES FOR ADMISSION.

The following have applied for admission to the Institute or transfer to another grade of membership, and in accordance with the By-laws the proposals will not be considered until the lapse of of least one month subsequent to the issue of this *Journal*, during which any Fellow, Member, or Associate Member may communicate by letter to the Secretary, for the confidential information of the Council, any particulars he may possess respecting the qualifications or suitability of any candidate.

The object of this information is to assist the Council in grading candidates according to the class of membership.

The names of the candidate's proposer and seconder are given in parentheses.

BOND, Douglas Harry, M.V.O., A.M.I.Mech. E., A.M.I.A.E., Lt.-Col., R.A.S.C. The War Office. (*S. J. M. Auld ; F. H. Garner.*)

GOLDSTEIN, Richard Frank, Ph.D., F.I.C. Research Chemist, Manchester. (*J. E. Haslam ; H. S. Kiernan.*)

GOODHIND, William Henry, Engineer, The Texas Oil Company Ltd., London. (*N. L. Anfilogoff ; P. H. Raimes.*)

HIRST, Norman, Student, Royal School of Mines. (*S. E. Coomber ; G. D. Hobson.*)

HUGHES, Fred, Junior Chemist, Manchester Oil Refinery Ltd. (*E. J. Dunstan ; R. Levi.*)

JENNINGS, W. Munro, jun., Chemist. (*R. F. Hurt ; W. M. Jennings.*) (*Application for transfer from Student.*)

TURNER, Eric Braybrooke, Student, Royal School of Mines. (*S. E. Coomber ; G. D. Hobson.*)

WARDLAW, Harold Wilberforce Roe, Exploitation Engineer, Apex (Trinidad) Oilfields Ltd., Trinidad. (*A. S. Taitt ; L. H. J. Hersch.*)

WILLIAMSON, David Kenneth Caird, B.Sc., Analytical Chemist, Shell Co. of Australia, Sydney, N.S.W. (*H. W. Stevenson ; F. Mackley.*)

ARTHUR W. EASTLAKE,
*Honorary Secretary.*

## REPLACEMENT OF *JOURNALS.*

*Journals* sent to overseas members may be lost or destroyed in transmission. The Council will be pleased to replace these free of cost, as far as stocks permit.

Members are asked to communicate with the Secretary if any of their *Journals* have not been received within about three months of the normal date of receipt.

## PAPERS IN THE *JOURNAL.*

The following Papers are scheduled for inclusion in the April issue of the *Journal.*

" Octane Rating Relationships of Hydrocarbons, etc.," by Dr. G. Egloff and P. M. Van Arsdell.

" Separation of Paraffin Wax. Part 4—The Sweating of Wax-Oil Mixtures," by M. F. Sawyer, T. G. Hunter, and A. W. Nash.

" Extreme-Pressure Addition Agents," by E. A. Evans and J. S. Elliot.

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# THE USE OF MINERAL OILS AS MOSQUITO LARVICIDES.*

By H. D. LORD, Ph.D., F.I.C.

SYNOPSIS.

A brief history of researches on the use of mineral oils for anti-malarial work is first given. A summary of Murray's recent investigations follows; perhaps the most important point he makes is that spreading pressure is all-important, and that toxicity is not nearly so crucial as had been previously accepted.

A description of the Adam–Langmuir apparatus for the measurement of surface pressure follows, and this is used extensively as a criterion of the quality of various anti-malarial oils. The effects of storage, exposure to diffused and bright sunlight, and addition of resin are described; also, limitations of the Adam apparatus, and the care which must be exercised in interpreting results therefrom are illustrated, with special reference to a used naphthalene extraction oil.

Essential requisites of a superior anti-malarial oil are next discussed, and finally it is shown that a residue from pressure distillate fulfils these requirements.

MALARIA is one of the best known of all fevers, and feared throughout the world, perhaps more by those who have never had it than by those who have. It is caused in the first place by infection from malaria-carrying mosquitoes, which breed and thrive best in hot countries, particularly in swampy areas where stagnant water and vegetation collect. A great deal of medical research has been carried out on the subject, and it is possible to alleviate or even prevent malaria, for instance by taking quinine, but the fever is always liable to recur unless the patient removes to and stays in a cold climate.

It has been calculated that in India alone over 1,125,000 deaths are caused annually from malaria, as well as a general deterioration in health and lowering in resistance to other diseases.

In the breeding-grounds the female mosquito lays eggs in the form of a long chain attached to a gelatinous material, which floats on the surface of water. In the normal course of events the eggs hatch out to larvæ in about three days, and the larvæ develop into mosquitoes over a somewhat longer period; these times are, however, dependent on factors such as temperature. There are, of course, many types of mosquito, including the anopheles, stegomyia, and culex, and they carry malignant forms of fever other than malaria. Any procedure, therefore, which can be devised to prevent or control the breeding of mosquitoes, as distinct from alleviation of fever caused by them, is of paramount importance.

One method of preventing the larvæ, which live under water but come periodically to the surface to breathe, from developing into full-grown mosquitoes is by spraying the surface of water with a suitable mineral oil. This penetrates the breathing-tubes of the larvæ, and kills them either by suffocation or by true toxic action. The development of the most suitable mineral-oil fractions for anti-malarial work is a subject which has occupied the active attention of this laboratory since 1926.

* Paper received 17th October, 1940.

From the number of anti-malarial oils on the market it would appear that other oil refiners have also been interested, but not many papers have been published on the subject. Several have dealt with insecticides and fungicides, but the intention is to confine this paper only to the use of mineral oils for anti-malarial work, remembering, of course, that in destroying malarial larvæ the carriers of other forms of fever are also eliminated.

## Review of Previous Publications.

A brief historical summary of the early development of anti-malarial oils is given in a book on malaria control by Covell.[1]

In 1928 Shutt [2] concluded that continuous oil films on water could not be obtained with straight mixtures of light and heavy petroleum fractions. The addition of small quantities of a 0·004 per cent. solution of NaOH in water or alcohol, however, caused the oil to spread evenly and rapidly. A satisfactory film was formed with 1 oz. of oil per 15 square feet of water.

From 1927 to 1930 Ginsburg [3] more fully investigated the use of petroleum fractions of different boiling ranges. He found that very light fractions such as benzine killed larvæ most quickly, but were too volatile to last, whilst high-boiling fractions were too viscous to penetrate the larval siphons or breathing-tubes. A suitable specification for a good anti-malarial oil was considered to be :—

| | |
|---|---|
| Sp. Gr. . . . | 30–34° Baumé—*i.e.*, 0·855–0·875. |
| Flash Point . . | 130–140° F. |
| Boiling Range . . | 350–740° F. (176–393° C.). |

Ginsburg also studied the tracheal penetration of oils by keeping larvæ and pupæ in water, under films of oil containing an oil-soluble dye in solution, followed by removal, washing, and examination under a microscope. He concluded that for efficient mosquito control the oil must not only form a uniform film on water, but must also be directly toxic to larvæ and pupæ, since in certain cases larvæ the respiratory siphons of which had been filled with non-toxic oils developed into adults.

Peterson and Ginsburg [4] showed that used crankcase oil, after straining and adding as a spread-aider either tar acid (containing 25 per cent. cresylic acid) or a light-petroleum distillate, could be used for anti-malarial work.

In 1931 Dr. Ramsay of the Ross Institute, India, collaborated first with the Assam Oil Co. and then early in 1932 with the Burmah Oil Co., at the Syriam Experimental Laboratory and up-country. The results of these investigations were recorded in a joint paper by Ramsay and Carpenter.[5] The necessary properties of anti-malarial oils were discussed and the results of field and laboratory work on a large number of petroleum fractions described. The general effect of boiling point and observations under the microscope were in agreement with Ginsburg's conclusions. As a result of the above investigations, formulæ for Assam and Burmah anti-malarial oils were adopted. Subsequent to 1932 field trials in India, the Straits, and the Federated Malay States have been conducted through the help and co-operation of the Principals of the Ross Institute of India.

In a series of three papers, Murray [6] gives the results of a fundamental investigation on larvicides. His work may be summarized as follows :—

(1) Pupation is prevented when oil penetrates larval tracheæ; it is therefore most desirable to produce a permanent stable oil film on water. An oil may give an unstable film because it contains polar substances, or because of unbalanced volatility of aliphatic and aromatic components.

(2) To ensure good film stability, a larvicidal oil should have either a low or a high aromatic content, and consist of wide and overlapping fractions; it may contain certain resins to assist its spreading power.

(3) The spreading power of an oil can be characterized by the determination of its surface pressure in the Langmuir–Adam apparatus. Pure paraffins are non-spreading and pure aromatics have a low spreading power. Tests in commercial larvicides indicate that spreading power is frequently due to impurities in the oil, and its value can be increased by irradiating the oil in thin layers.

## Experimental.

The composition of the anti-malarial oil produced in India and Burma by the Assam Oil Co., Ltd., and the Burmah Oil Co., Ltd., often referred to in this paper as " Malariol "—this being the brand name under which it is sold—remained constant for a number of years. The oil gave quite satisfactory service in several spheres, and many favourable reports as to its efficiency were received. Nevertheless, it was considered that it should be capable of improvement, and the present paper includes an account of experiments carried out with that aim in view.

## Adam's Surface-Pressure Apparatus.

Spreading of an oil on water is dependent on surface tension. It occurs if the sum of the air–oil surface tension and the water–oil interfacial tension is less than the air–water surface tension. Expressed mathematically, where $T$ is the tension in dynes/cm. we have :—

Spreading occurs if,

$$T \text{ air/oil} + T \text{ water/oil} < T \text{ air/water}.$$

Since for a clean water surface the value $T$ air/water is constant, there is a sharp transference from the condition of " no spread " to " spread " as the surface tension of the oil is lowered. There are complications if the water surface is dirty, and the change over is not nearly so sharp, but for a clean surface the spreading power of an oil can be measured precisely by the amount in dynes/cm. by which the right-hand side of the above expression exceeds the left—*i.e.* :—

$$\text{Spreading power (dynes/cm.)} = T \text{ air/water} - (T \text{ air/oil} + T \text{ water/oil}).$$

It is possible to measure the tendency to spread, or spreading pressure, of an oil quite accurately and rapidly, using a very small quantity, with the aid of the Adam–Langmuir surface-pressure apparatus.[7] This consists of a shallow brass trough which is filled with pure water. Near one end

there is a light floating barrier attached to a calibrated scale. The sides of the trough, the floating barrier, and a glass barrier which can be placed at any measured distance from this floating barrier are all lightly waxed to prevent leaks. If an oil is now placed on the surface of the water it exerts a pressure on the floating barrier which can be measured on the calibrated scale.

The method adopted here for the measurement of surface pressure of anti-malarial oils has followed closely that used earlier by Murray, who found that oleic acid provided a suitable buffering film for all pressures up to about 30 dynes/cm. If the trough is filled with water and the glass barrier placed near the opposite end of the floating barrier, then, on covering the surface of the water with oleic acid, a certain pressure is exerted on the floating barrier which is transmitted to and measured on the calibrated scale. By moving the glass barrier along the trough, the pressure exerted by the film of oleic acid on the floating barrier can be increased gradually, until finally at about 30 dynes/cm. the film collapses.

In measuring the surface pressure of anti-malarial oils a film of oleic acid at a certain pressure is first produced on the trough. This is effected by dropping on to the water surface 0·2–0·3 c.c. of a solution of 1 part oleic acid in 1000 parts ordinary petroleum ether, and waiting 5 minutes for the latter to evaporate. A small drop of oil is then allowed to fall on the surface, and if it spreads it means that it exerts a pressure greater than that of the oleic acid. The glass barrier is then moved to give a higher pressure on the oleic acid film, and another drop of oil allowed to fall as before. This procedure is repeated until the oil-drop just fails to spread, which means that its surface pressure or tendency to expand is just counterbalanced by that of the oleic acid. If no spreading takes place with the first drop of oil, the barrier is moved in the opposite direction to ascertain the neutral point.

By the above method it is possible to measure the spreading pressures of anti-malarial oils with precision.

It is desirable not to allow the oil to touch the float, the waxed barriers, or the sides of the trough, as otherwise wax is dissolved. Consequently the number of drops on the surface at any one time should be limited to about eight. After an experiment the oil can be removed from the surface by placing a wax glass barrier between the float and the nearest drop, and then compressing the film until all the drops occupy a small area, when they can be removed by absorbing carefully with filter-paper. If the spreading pressure of an oil under test exceeds the collapsing pressure of the oleic acid film, the oil immediately covers the whole of the surface, and cannot be compressed back into a lens. In this case the whole apparatus has to be cleaned and rewaxed.

Fuller particulars of the original calibration of the apparatus and method of routine testing are given in the appendix.

## Results.

The spreading pressures of several samples of larvicidal oils are given in Table I.

Spreading pressures of all anti-malarial oils tested showed a tendency

TABLE I.

*Spreading Pressures of Anti-Malarial Oils Determined on* 16.2.39.

| Oil. | Date Received. | Spreading Pressure, dynes/cm. |
|---|---|---|
| (1) Malariol after 3 months' storage in the dark | — | 22·8 |
| (2) Sample A | 5.3.38 | 22·1 |
| (3) Sample B | 5.3.38 | 19·5 |
| (4) Sample C | 12.9.38 | 18·2 |
| (5) Sample D | 12.9.38 | 16·9 |
| (6) Sample E | 12.9.38 | 15·3 |
| (7) Sample F | 5.5.37 | 28·7 |
| (8) Malariol | Early 1937 | 26·1 |

to increase with time, so that a sample of Malariol after 3 months' storage was chosen for comparison with the other still older products tested. It will be seen that its spreading pressure is well above the average, and this, together with its good toxic properties, no doubt accounts for the fact that it has been largely successful in the past.

## EFFECT OF TIME.

Malariol *as made* varied in spreading pressure from 15 to 18 dynes/cm. After about 3 months' storage it was considerably higher, as shown by the particular sample in Table I at 22·8 dynes/cm., whilst after 2 years it could reach a figure of over 26 dynes/cm. Such a gradual increase in spreading pressure with time is typical of all oils examined by us, although of course the magnitude of such increase varies according to the nature of the particular product considered, and means that such anti-malarial oils improve in storage. This must be due to minor reactions, since normal physical properties apart from tint are unaffected; it confirms that good spreading pressure depends mainly on low concentrations of "impurities." Depending on how long Malariol takes to reach the consumer after being made, it suggests that the possibility of storage in the refinery for say 3 months prior to despatch may be considered with advantage.

## EFFECT OF SUNLIGHT.

A sample of Malariol which had a spreading pressure of 22·7 dynes/cm. was taken in three test-tubes; one was kept in the dark, a second in diffused light, and the third in direct sunlight. After four days, spreading pressures were measured again, and the results obtained are given in Table II.

TABLE II.

*Change in Spreading Pressure dynes/cm. of Malariol after Exposure for* 4 *Days in Test-tubes.*

| Original. | Dark. | Diffused Light. | Sunlight. |
|---|---|---|---|
| 22·7 | 22·7 | 23·2 | 24·0 |

The same sample of Malariol was exposed in very thin films by placing 3 c.c. at a time in flat-bottom dishes 4 inches in diameter. Changes were very much more rapid.

TABLE III.

*Change in Spreading Pressure dynes/cm. of Malariol after Exposure in Thin Films for 18 Hours.*

| Original. | Dark. | Diffused Light. | Sunlight. |
|---|---|---|---|
| 22·7 | 22·9 | 26·3 | >30 |

The above results indicate the distinct possibility of producing a marked improvement in anti-malarial oils by irradiation with artificial light. It is hoped to study this effect in detail at a later date.

EFFECT OF SUNLIGHT ON THIN FILMS OF MALARIOL ON WATER.

3 c.c. of the above Malariol with a spreading pressure of 22·7 dynes/cm. were spread on 1000 c.c. of distilled water in a clean glass desiccator; the surface of the water was 8 inches in diameter. After exposing to direct sunlight for 4 hours it was noticed that the water became turbid, and the turbidity increased with time. At the end of 3 days the oil layer was collected and the spreading pressure measured; it was found to be very much in excess of 30 dynes/cm. About 0·2 c.c. of oil was extracted from the turbid water, and this also had a spreading pressure of over 30 dynes/cm. No turbidity was produced in a similar experiment after several days' exposure on a laboratory bench in ordinary diffused light.

This marked susceptibility of Malariol to sunlight, and consequent large increase in spreading pressure, is quite advantageous, since it means that once spread on water any such action due to exposure will be very helpful. It was decided to test also the effect on toxicity.

Toxicity tests on a sample of Malariol are given in Table IV. These were obtained in the normal way by placing the larvæ in an enamel basin 9 inches in diameter, almost full of water, and dropping from a pipette on to the surface 0·7 c.c. of Malariol, equivalent to 4 oz. per 100 square feet, the amount recommended for field use. This was chosen as the starting-point, and the time taken in minutes for the first larvæ to be forced perma-

TABLE IV.

*Duplicate Toxicity Tests on Typical Sample of Malariol.*

| | Anopheles (Mts.). | | Stegomyia (Mts.). | |
|---|---|---|---|---|
| | (1). | (2). | (1). | (2). |
| First one down in . . | 1½ | 2 | 4 | 2 |
| 50% ,, . . | 2½ | 4 | 6 | 4 |
| All ,, . . | 12 | 12 | 15 | 14 |

nently to the bottom noted; the 50 per cent. and 100 per cent. points were also recorded in like manner.

20 c.c. of the above Malariol were spread on the surface of 8000 c.c. of water in an aspirator bottle 9 inches in diameter. The bottle was kept in direct sunlight for 3 days; as before, the water became turbid towards the end of the first day. The oil on the surface, which had been bleached considerably, was collected, and results of toxicity tests on this sample are given in Table V.

TABLE V.

*Duplicate Toxicity Tests of Malariol Collected from a Water Surface after 3 Days' Exposure to Sunlight.*

| | Anopheles (Mts.). | | Stegomyia (Mts.). | |
|---|---|---|---|---|
| | (1). | (2). | (1). | (2). |
| First one down in . . | 1½ | 2 | 1½ | 1 |
| 50% „ . . | 2 | 3 | 2 | 1½ |
| All „ . . | 3½ | 5 | 5 | 8 |

On comparing the results in Tables IV and V, it will be observed that exposure to sunlight not only increases the spreading power of Malariol, but also has a markedly beneficial effect on the toxicity.

## CONTAMINATION OF WATER.

Any anti-malarial oil should as far as possible be insoluble in water, so that in use in the field, the water on which it is sprayed should remain non-toxic to fish, and non-injurious to animals, birds, and humans. It has been seen that although Malariol as made is almost totally insoluble in water, nevertheless on exposure to direct sunlight, reactions take place and a minor portion may dissolve, which in a very limited amount of water can produce turbidity. It was decided to test this contaminated water for toxicity. Both anopheles and stegomyia were introduced into the water in separate basins, and although some died, most of them were alive overnight, and many developed into mosquitoes. It follows that even with a very limited amount of stationary water plus bright sunshine, the soluble products are not very toxic, and in normal field use, where much greater volumes, often not stagnant, are involved, the danger due to contamination in this way should be negligible.

## MAINTENANCE OF STABLE FILMS.

The major importance of spreading power in any anti-malarial oil has already been stressed, and the ease with which spreading pressure can be measured by the Adam–Langmuir apparatus described, with a few typical results. It is desired to stress even more forcibly here, however, that although the above apparatus has proved of very great value in the present investigation, every care must be taken in interpreting specific results therefrom obtained at any time and in any centre. It only gives the

spreading pressure of any particular sample at the time of test, and gives no indication of what may happen to a film of oil after its initial spread, due either to chemical reactions on exposure to light, or to solubility of certain constituents in water. Moreover, the maintenance of a stable film of oil over a long period is of the utmost importance.

A typical example where measurement of spreading pressure alone might lead to completely erroneous conclusions has been afforded here recently. A sample of diesel oil which had been used for the extraction of naphthalene was examined for its larvicidal qualities, and gave the results shown in Table VI.

TABLE VI.

*Comparison between Diesel Oil used for Naphthalene Extraction and Malariol.*

| | Malariol. | Used Diesel Oil. |
|---|---|---|
| Sp. Gr. 60° F. . . . | 0·913 | 0·892 |
| I.B.P., ° C. . . . . | 224 | 156 |
| 10% distilled under . . | 265 | 209 |
| Spreading pressure, dynes/cm. | 24 | 28 |
| Stability of film . . . | An unbroken and effective film of oil covering the whole surface of water for a period of over 3 days is produced. | The oil spreads quickly, covering the whole surface of water, but after about 5 minutes the film breaks up into lenses. Within a short time the lenses join to form patches of oil, leaving the water surface almost clear. After 10 or more hours the oil tends to spread again, but does not produce a good or stable film. |

*Toxicity Test.*

| | Anopheles. | Stegomyia. | Anopheles. | Stegomyia. |
|---|---|---|---|---|
| First one down in . | 2 mins. | 5 mins. | 2 mins. | 7 mins. |
| 50% ,, . | 5 mins. | 7 mins. | 5 mins. | 14 mins. |
| All ,, . | 10 mins. | 11 mins. | Approximately 1½ hrs. | 50% alive after 3 hrs. |
| | | | and a few quite active even after 24 hrs. | |

The used diesel oil gave a high spreading pressure as measured by the Adam apparatus, and this accounted for its excellent *initial* spread on water. The subsequent behaviour of the oil was, however, both interesting and damning. After about 5 minutes, due largely to the naphthalene content as shown by special trials in which naphthalene was deliberately added to Malariol, the film broke up into large lenses which joined to form patches, leaving an almost clear surface of water where larvæ thrived for at least 24 hours. After the lensing the naphthalene present in the oil evaporated slowly, taking under laboratory conditions 10–12 hours; the oil then tended to spread again, but it did not produce a good film or one which was injurious to larvæ.

It follows from the above that the oil in question is not at all suitable

for anti-malarial work in spite of its high initial spreading pressure, and the example illustrates clearly the care which must be exercised in interpreting results obtained with the Adam apparatus.

## Toxicity.

Murray was probably the first to point out that toxicity in anti-malarial oils was not nearly so important as had been previously surmised, and that once an oil penetrated the tracheal system of larvæ, pupation never took place.

Experiments here with non-toxic aromatic-free kerosine have confirmed this view, but in certain cases larvæ have remained alive for over 10 days. It follows that, although true toxicity is not strictly essential, it does have a very pronounced effect on the speed of action of an oil on larvæ.

## Viscosity.

Viscosity is another factor on which depends to a great extent the effective action of anti-malarial oils. Penetration into the larvæ siphons is all-important, and this can only take place if the viscosity of the oil is reasonably low. It is possible, for example, for larvæ to live several days under a film of highly toxic aromatic extract from a lubricating oil base, because the viscosity of the oil is too high for effective penetration into the trachea.

## Evaporation.

Although an oil has to be fairly thin to penetrate tracheal tubes, it must not be unduly volatile. If it is, evaporation quickly takes place when it is spread on a water surface, and apart from alteration in composition and therefore spreading pressure, also stability of film, the viscosity increases, and the oil may become too thick for effective action. A useful arbitrary figure for volatility may be obtained by heating in an oven, maintained at 100° F., through which a steady flow of air passes. From experiments here it would appear that the initial boiling point of an anti-malarial oil should be well over 200° C., and preferably near 250° C.

## Effect of Resin.

It is a well-known fact that resinous substances increase the spreading power of oils. The quantitative effect on a kerosine extract and on Malariol is illustrated in Table VII.

**Table VII.**

*Effect of Resin on Spreading Pressure.*

| Oil. | Spreading Pressure, dynes/cm. | Resin, %. | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | 0·1. | 0·2. | 0·25. | 0·3. | 0·5. | 1·0. | 2·0. | 3·0. |
| A kerosine extract . | 14·0 | 17·1 | 20·4 | 22·4 | — | 25·8 | 26·3 | 27·6 | 28·1 |
| Malariol . | 21·6 | 24·5 | 26·8 | — | 28·4 | — | — | — | — |

Although spreading pressures are increased markedly, the effect of resin on other factors, such as stability of film and contamination of water, is not known. These have not been investigated, as the improved Malariol referred to later would appear to be satisfactory for all purposes, without the trouble and expense of adding a special foreign agent.

## Characteristics of Anti-Malarial Oil.

The requisites are as follows :—

(1) A fairly high spreading pressure to produce an immediate, unbroken, and effective film when sprayed on water at a rate equivalent to 4 oz. per 100 square feet.

(2) The film produced must remain stable and effective over a long period. After final evaporation it should not leave permanent residual deposits.

(3) The viscosity must be fairly low, so that larval trachea are easily penetrated.

(4) The oil must not contain very volatile ingredients which on evaporation will leave the film thick and non-penetrating, or alternatively cause segregation into lenses.

(5) Ingredients which either by evaporation or solubility in water affect the stability of the film adversely are to be avoided.

(6) The oil should possess true toxic properties, since although these are not technically essential, a quick "kill" of larvæ is likely to prove the best demonstration of its efficacy to the ordinary layman and consumer.

(7) It should be non-toxic to fish, birds, animals, and humans. This applies especially to any components which may be soluble in water.

(8) The oil should be fairly dark in colour so that thin films on water are clearly visible.

It may be stated at once that the original Malariol passed the above criteria fairly satisfactorily, but its spreading pressure might have been improved a little with advantage; at times it was too volatile with an I.B.P. below 200° C., and it was not dark enough to give a clearly visible film in all cases. Moreover, according to Murray's work, its constitution was quite wrong, since it contained approximately 50 per cent. of aromatics of a boiling range similar to the non-aromatics.

It was decided to study the properties of blends of a residue from pressure distillate with : (*a*) a kerosine extract, (*b*) an extract from a lub. base of low cold test, (*c*) an extract from a lub. base of high cold test.

These extracts were all normal works products.

P.D. Residue was chosen as the base oil because it was relatively cheap, of about the right boiling range and viscosity, was quite toxic, and had a high spreading pressure which increased with time.

## Spreading Pressure.

Blends were made from samples which had been stored for 3 months; it has been shown previously that spreading pressures and toxicity increase

with time; and if Malariol does not always take 3 months to reach the consumer, it should be stored longer in the refinery before despatch. Spreading pressures were first determined, and the results obtained are recorded in Table VIII, and graphically in Fig. 1.

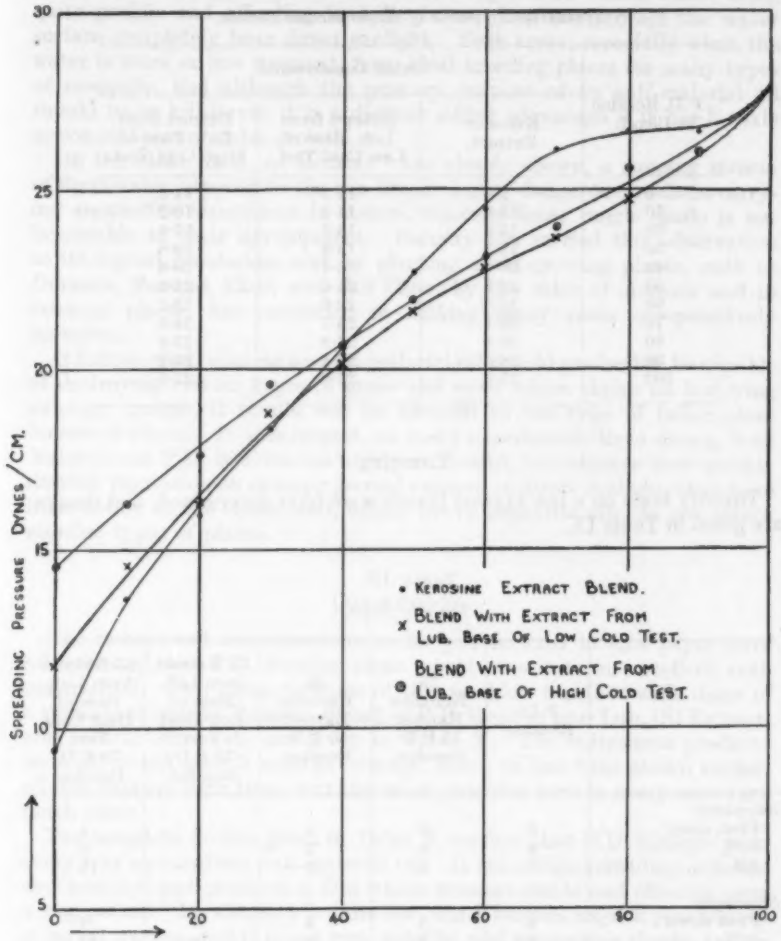


FIG. 1.

In all cases the spreading pressure increases fairly gradually to a maximum value with increase in content of P.D. Residue. It follows that from this point of view alone—and it has been shown that good spreading

is probably the most important of all requirements for a good anti-malarial oil—the P.D. Residue content should be as high as possible.

TABLE VIII.

*Spreading Pressures of Experimental Blends.*

| % P.D. Residue in Blend. | Other Constituents. | | |
|---|---|---|---|
| | Kerosine Extract. | Extract from Lub. Base of Low Cold Test. | Extract from Lub. Base of High Cold Test. |
| 0 | 9·4 | 11·7 | 14·5 |
| 10 | 13·6 | 14·5 | 16·2 |
| 20 | 15·9 | 16·2 | 17·6 |
| 30 | 18·3 | 18·8 | 19·6 |
| 40 | 20·4 | 20·1 | 20·6 |
| 50 | 22·7 | 21·6 | 21·9 |
| 60 | 24·5 | 22·9 | 23·2 |
| 70 | 26·1 | 23·7 | 24·0 |
| 80 | 26·6 | 24·8 | 25·6 |
| 90 | 26·6 | 26·1 | 26·1 |
| 100 | 27·9 | 27·9 | 27·9 |

## TOXICITY.

Toxicity tests on a few typical blends were next determined, and results are given in Table IX.

TABLE IX.

*Toxicity Tests.*

| | P.D. Residue. | 25 Kerosine Extract 75 P.D. Residue. | 50 Kerosine Extract 50 P.D. Residue. | 25 Extract from Lub. Base of Low Cold Test 75 P.D. Residue. | 25 Extract from Lub. Base of High Cold Test 75 P.D. Residue. |
|---|---|---|---|---|---|
| *Anopheles.* | | | | | |
| First down . . | 3 | 3 | 3 | 4 | 4 |
| 50% „ . . | 4 | 5 | 5 | 7 | 8 |
| All „ . . | 7 | 8 | 9 | 9 | 16 |
| *Stegomyia.* | | | | | |
| First down . . | 4 | 5 | 4 | 5 | 7 |
| 50% „ . . | 6 | 8 | 6 | 8 | 11 |
| All „ . . | 12 | 16 | 10 | 13 | 19 |

These results show that P.D. Residue is highly toxic, and that from the point of view of this criterion there is no necessity whatever to incorporate any other ingredient in Malariol; this is in accord with the results in the previous section for spreading pressures.

## Effect of Vegetation.

The effect of vegetation on larval growth is somewhat varied.

In many places in the tropics, particularly during monsoon seasons, low-lying water-logged ground abounds in vegetation, which, whilst being quite prolific and affording food for larvæ, does not protect the water surface completely from direct sunlight. Such areas, especially when the water is more or less stagnant, form ideal breeding-places for many types of mosquito, and although the primary purpose of an anti-malarial oil should be to kill larvæ, it is a distinct added advantage if it has a toxic action on this vegetable growth.

On the other hand, as Ramsay [8] has clearly shown, a running stream of flood-water exposed to the sun breeds highly dangerous, malaria-carrying anopheline mosquitoes in Assam, whereas dense jungle shade is unfavourable to their development. Ramsay has carried this observation to its logical conclusion, and by planting quick-growing plants, such as Duranta, Tarapat Ekor, and Jali Cane, by the sides of streams and in swampy places, has succeeded in making many areas comparatively harmless.

It follows that whereas an anti-malarial oil should preferably be capable of destroying certain types of grass and weed which thrive on low-lying swampy ground, it should not be harmful to the type of taller plant indicated above. In this respect, as many experiments have shown, both Malariol and P.D. Residue are highly successful, for, whereas they quickly destroy vegetation on swampy ground exposed to direct sunlight, they have little action in the shade, and, unlike heavy asphaltic oils, do not attack sturdier types of plants.

## Conclusions.

The results and considerations so far put forward in this paper have all indicated that P.D. Residue alone would constitute an excellent anti-malarial oil. Full characteristics of this product, together with those of a typical old quality Malariol, blends of P.D. Residue plus Lub. Oil Extract, and several other oils, are given in Table X. The indigenous products were all tested after 3 months' storage, since, as has been shown earlier, all oils improve with time, and the other products were in every case very much older.

The complete results given in Table X confirm that P.D. Residue is in every way an excellent anti-malarial oil. It has a high spreading pressure and toxicity, and produces a film which remains stable and effective over a long period. Its viscosity is quite low, which ensures a quick penetration of larval trachea, but it is not very volatile, and evaporates slowly, taking over 3 days in exposed areas. The oil improves markedly in storage, and particularly on exposure to sunlight. It is relatively non-toxic to fish, birds, animals, and humans, but has quite a powerful destructive action on unwanted vegetation.

Malariol produced from P.D. Residue is superior to the former Malariol in that, whilst being similar in other properties, it is a little darker, has a very much higher spreading power and at least equal toxic action. As

TABLE X.

*General Characteristics of Anti-Malarial Oils.*

| | Indigenous Oils. | | | | | Non-indigenous Oils. | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | P.D. Residue. | 50 Kerosine Extract 50 P.D. Residue. | 25 Kerosine Extract 75 P.D. Residue. | 25 Extract from Lub. Base of Low Cold Test 75 P.D. Residue. | 25 Extract from Lub. Base of High Cold Test 75 P.D. Residue. | A. | B. | C. | D. | E. | F. |
| Date received | 19.5.39 | 19.5.39 | 19.5.39 | 19.5.39 | 19.5.39 | 5.3.38 | 5.3.38 | 12.9.38 | 12.9.38 | 12.9.38 | 5.5.37 |
| Sp. Gr., 60° F. | 8635 | 9092 | 8880 | 9275 | 9262 | 8510 | 9275 | 8935 | 8910 | 8750 | 858 |
| I.B.P., ° C. | 244 | 225 | 243 | 253 | 253 | 220 | 220 | 188 | 214 | 229 | 230 |
| 10% distilled under ° C. | 257·5 | 256·5 | 257 | 262 | 262 | 245 | 269 | 219 | 233 | 252·5 | 252·5 |
| 20% " " | 263 | 263 | 263 | 270 | 268·5 | 258 | 306 | 236 | 246 | 265 | 264 |
| 30% " " | 268 | 268 | 268·5 | 276 | 276 | — | — | 247 | 255 | 275 | 274 |
| 40% " " | 272·5 | 273 | 273 | 283 | 284 | — | — | 257·5 | 264 | 284 | 283 |
| 50% " " | 278 | 276·5 | 279 | 294 | 294 | 286·5 | 372 | 268 | 274 | 294 | 292·5 |
| 60% " " | 285 | 282 | 284 | 305 | 305 | 290 | 382 | 280 | 287 | 306 | 302·5 |
| 70% " " | 292·5 | 288 | 290·5 | 323 | 324 | — | — | 300 | 305 | 318 | 315·5 |
| 80% " " | 302 | 296 | 300 | 353 | 353 | — | — | 336 | 337 | 338 | 333 |
| 90% " " | 319·5 | 313 | 319 | — | — | 368 | 400 | — | — | — | 368 |
| % distillate under : | | | | | | | | | | | |
| 225° C. | — | — | — | — | — | 1·0 | 1·0 | 2·0 | 4·5 | — | — |
| 250° C. | 3·5 | 5·5 | 3·0 | 1·0 | 1·0 | 14·0 | 6·0 | 13·5 | 24·5 | 9·0 | 7·5 |
| 275° C. | 45·5 | 46·5 | 44·0 | 29·0 | 29·5 | 38·0 | 12·0 | 32·5 | 51·5 | 30·0 | 32·5 |
| 300° C. | 78·5 | 84·0 | 80·0 | 56·0 | 56·5 | 62·0 | 18·5 | 57·5 | 68·0 | 56·5 | 57·5 |
| Spreading pressure, dynes/cm. | 27·5 | 22·8 | 26·3 | 24·2 | 24·8 | 22·2 | 19·6 | 18·3 | 16·9 | 15·4 | 28·4 |
| Spreading pressure determined on | 18.8.39 | 18.8.39 | 18.8.39 | 18.8.39 | 18.8.39 | 16.2.39 | 16.2.39 | 16.2.39 | 16.2.39 | 16.2.39 | 16.2.39 |
| Evaporation test at 100° F. for 16 hrs. (loss % by wt.) | 4·2 | 6·3 | 5·9 | 4·9 | 6·2 | 11·9 | 5·8 | 22·6 | 20·1 | 9·0 | 9·2 |
| Toxicity tests on : | | | | | | | | | | | |
| Anopheles (A) and Stegomyia (S) | A. S. | A. S. | A. S. | A. S. | A. S. | A. S. | A. S. | A. S. | A. S. | A. S. | A. S. |
| Total number of tests | (6) (9) | (13) (16) | (3) (3) | (3) (3) | (5) (5) | (3) (5) | (2) (3) | (3) (4) | (4) (6) | (2) (2) | (2) (2) |
| Average results : | | | | | | | | | | | |
| First larvæ down, mins. | 3 4 | 3 4 | 3 5 | 4 5 | 4 7 | 7 9 | 4 13 | 4 6 | 3 8 | 3 5 | 4 8 |
| 50% " " " | 4 6 | 5 6 | 5 8 | 7 8 | 8 11 | 10 17 | 14 35 | 8 13 | 6 18 | 9 18 | 7 16 |
| All " " " | 7 12 | 9 10 | 8 16 | 9 13 | 16 19 | 25 42 | 28 59 | 13 30 | 11 42 | 17 44 | 15 37 |

N.B.—It is difficult to obtain larvæ at different times, or even at the same time, with constant powers of resistance; consequently toxicity tests are only indicative of general relative values, and are not absolutely accurate.

Table X shows, some of the products examined are in fact quite poor, with relatively low spreading powers, high volatilities, and rather low toxicities. The only oil nearly approaching Malariol made from P.D. Residue is sample F, but even this has a rather high evaporation loss, and relatively poor toxicity, while its high spreading pressure may be due largely to the fact that it was well over 2 years old when tested. The spreading pressure of Malariol P.D. Residue exceeds 30 dynes/cm. after only 4 months' storage.

The Author is indebted to the Directors of The Burmah Oil Co., Ltd., for permission to publish this paper, and wishes to acknowledge the help of Mr. K. V. Baskaran in the practical work involved.

*Experimental Laboratory,*
*Syriam,*
*Burma.*

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## APPENDIX.

### (*a*) Care and Manipulation of Adam's Surface Pressure Apparatus.

(1) The brass trough should be scrupulously clean; before starting a series of experiments it is waxed by placing in the steam oven for half an hour and then painting with molten 125/30 White Wax, using a camel-hair brush.

(2) The platinum barriers and the underside of the float of the instrument are lightly waxed to prevent leakage. For this purpose a solution of 125/30 wax in light petroleum spirit is suitable, and 3–4 hours should be allowed for drying.

(3) Having placed the instrument on the trough, fill the latter with distilled water $P_H$ 6·0, and level it by means of the screw legs provided.

(4) Loosen the jaws clamping the copper float, taking care to see that it has an unimpeded movement. The lower jaws of the clamp should be fully submerged, to ensure complete freedom of movement of the float.

(5) Move the waxed barriers across the surface from the float towards the opposite end of the trough, to make sure that the surface is clean.

(6) Adjust the light from the lamp so that it is reflected from the mirror on the float mechanism back on to the vertical scale. Choose an arbitrary position of the spot so that the float may be brought back to the same position every time it is displaced.

(7) After calibration, measure the surface pressure as indicated in the text of this report.

### (*b*) Calibration.

#### (1) *Experimental.*

To calibrate the instrument, bring the pointer arm to zero on the semi-circular vertical scale, and suspend the aluminium tray from the horizontal arm attached to the upper torsion wire.

Bring the reflected light back to zero by turning the lower milled head, to which is attached the lower torsion wire.

Carefully remove the tray and bring the spot of light on the vertical scale back to zero by means of the pointed on the semi-circular vertical scale on the instrument. The aluminium tray weighs 0·1 gram, hence the reading now taken on the semi-circular scale in degrees is for 0·1 gram. The same procedure is repeated for 0·2 and 0·3 gram by adding the necessary weights to the tray.

(2) *Calculations.*

The apparatus is constructed in such a way that for a given reading on the scale the force $P$ acting on the floating barrier of effective length $L$ at a distance $l$ from a fulcrum is balanced by a mass $m$ also at a distance $l$ from the fulcrum. Therefore taking the moments we have :—

$$P \times L \times l = m \times g \times l$$

and

$$P = \frac{m \times 981}{L}.$$

Using different weights it is possible to calculate the force corresponding to each degree division on the scale. In the Syriam machine 1° is equivalent to a spreading pressure of 0·26 dyne/cm.

## *CONTRIBUTED DISCUSSION ON DR. LORD'S PAPER.*

Dr. M. Y. Young writes :—

Dr. Lord is to be congratulated on his excellent paper.

What would be of interest to know is how Malariol would behave in other fields than Assam, Burma, or Federated Malay States under different atmospheric conditions and at varying seasons of the year, as, for instance, in Iran. Dry heat at one time, humidity at another, may affect the composition of the larvicide. Volatility in dry heat was one of the great disadvantages of oil larvicides in my experience in Iran, the evaporation which took place increasing viscosity with resulting "islet" formation on the surface of the water and consequent freedom for larvæ to breed. I do not know how far Dr. Lord's laboratory experiments in this respect would satisfy these requirements in the actual fields of operation geographically distributed at various seasons, and I would suggest that a supply of Malariol should be despatched to Iran for trial tests in the Company's fields there.

Surface tension is, admittedly, all-important in the efficacy of an anti-mosquito oil, but it would seem to me, as indeed it would to the average layman and consumer, that toxicity in a larvicide is as important, and cannot be passed over lightly. The function of a mosquito larvicide should be to destroy the larvæ, as the surest means of preventing pupation. Whether by penetration through the tracheal system or in other ways, the larvæ should be killed in a reasonable time, and no chances should be taken about it. It is, therefore, gratifying to know that Dr. Lord has devoted attention to toxicity as the primary object of a larvicide like Malariol, however desirous it may be to render it innocuous in other directions for specific reasons. It is common knowledge that larvæ thrive principally in stagnant waters; unless such waters can be drained or otherwise removed, they should be rendered unfit for larvæ to breed in, regardless of other considerations, such as vegetable or animal life. The former, more often than not, assists larval growth; the latter are, more often than not, incapable of completely destroying it. As for drinking-water for human and animal consumption, there are generally other sources of supply or other means of dealing with it.

Professor N. K. Adam, F.R.S. (*University College, Southampton*) :—

Dr. Lord is to be heartily congratulated on a very thorough and clear account of the essentials of the problem of producing a satisfactory oil film for killing mosquito larvæ.

The instrument which he has used for determining the spreading pressure, designed by Jessop and myself in 1925, is accurate, but for many purposes may be unnecessarily elaborate. Simpler instruments with only one torsion wire instead of two are easily made, and give an accuracy of about 0·3 dynes per cm., which is good enough for most purposes, and this accuracy might, if necessary, be increased somewhat.

There is also a very simple and rapid method of comparing the spreading pressure of two oils, which involves very little apparatus, merely a set of oils or mixtures of known spreading pressure, determined by a surface pressure balance in the manner indicated by Dr. Lord and Dr. D. R. P. Murray. A clean surface of water is produced at the top of a glass funnel six or more inches in diameter, by running water in for some time from the stem and sweeping the contamination over the rim with the overflowing water. The inflowing water is then stopped, and a drop of each oil, that of known and that of unknown spreading pressure, placed on different parts of the clean surface. The oil with the larger spreading pressure rolls back the film of the other, which remains as a lens on the surface, only the oil of larger spreading pressure spreading out to a film. Suitable oil mixtures have been described by myself, dodecyl alcohol and a white, non-spreading mainly paraffinic oil (*Proc. Roy. Soc.*, B, **122**, 134 (1937)). As the concentration of the dodecyl alcohol is increased from zero to one per cent., the spreading pressure increases from zero to 22 dynes per cm. The mixtures of ethyl myristate and medicinal paraffin described by Norris and Taylor (*J. Chem. Soc.*, 1938, 1719) are equally suitable, but require much larger amounts of the rather rare ethyl myristate. Oleic acid is sometimes recommended as giving a standard and higher spreading pressure, but suffers from the serious disadvantage that changes in acidity in the water, such as frequently occur in practice, very considerably affect the spreading pressure of any substance with an acidic end group. In the field, given a set of small bottles of one or other of these mixtures, it should be possible to determine the spreading pressure of an unknown oil within about one or two dynes per cm. If there are soluble but surface-active substances in the water, the spreading pressure may be much increased, but this is not very likely to occur in the field. "Medicinal" paraffin can be substituted for the white oil used in my work.

I do not think that the factors determining the stability of the thick oil films required to kill larvæ is yet fully understood. I agree, however, with Dr. Lord in thinking that, with the types of oil likely to be used for anti-malarial purposes, evaporation or solution of some important constituent is largely responsible for the break-up into lenses and an extremely thin film, probably one molecule thick. A quite insoluble pure substance, however, almost always forms an extremely unstable thick film; spreading takes place very rapidly to a film of visible thickness, which almost immediately breaks up into thick lenses and a monomolecular film between. Why mixtures of oils such as ordinary kerosine and Malariols should form thick films stable for a very long time does not yet seem clear.

LIEUT. G. I. WATSON, M.D., M.R.C.S., D.T.M. & H., writes:—

It is of real interest to read Dr. Lord's observations on pressure distillate residues, and his conclusion that "P.D. residue is in every way an excellent anti-malarial oil." His remark that it is relatively cheap shows that we can all agree on this most important "property" of an anti-malarial oil. Indeed, it would be instructive if, in all tables of general characteristics of anti-malarial oils, such as Table X here, a column were added to show the local cost of each oil or mixture.

The most important attribute of any anti-malarial technique is its cost. This is as true of oiling as of subsoil drainage. Lower the cost of an oil, and there is a real gain to offset any slight drop in efficiency; increase the cost for a small gain in efficiency, and you may lose the market.

That Dr. Lord does not, however, fully appreciate the physiological problem of how most cheaply to rid a flowing stream of anopheline larvæ is shown by two sentences of his paper: "... malaria-carrying mosquitoes, (which) breed and thrive best in hot countries, particularly in swampy areas where stagnant water and vegetation collect." and "Characteristics of Anti-Malarial Oil ... (2) The film produced must remain stable and effective over a long period." It would be interesting to know whether more swamp-breeding or stream-breeding malaria carriers are controlled by oiling. This swamp-mindedness has obstructed clear thinking on many aspects of malaria control, but on none more than oiling. So many workers have sought after that El Dorado, the permanent film, which "under the conditions in which anti-malarial oils are used (permanency) is as often as not impossible to obtain." This is a sentence from a letter by Sir Malcolm Watson, Director of the Ross Institute, emphasizing again that fact which he discovered in 1914, when he first used oil to control mosquitoes breeding in running water. When one who is swamp-minded approaches the matter

of spread of an anti-malarial oil, he conjures up an ideal oil which spreads to the limits of Space and endures to the limits of Time.

This mighty oil film would indeed control mosquito-breeding; but, fortunately for the sanitarian, some lesser oils do so too, such as the various "Malariol" products. They do so in streams as well as in swamps. They may be used sometimes as an emulsion or as a surface film. They kill mosquitoes and their larvæ, not only because of this or that fraction in their formula, but because they are oils and because mosquitoes were not built to live in oil.

A paper which will appear in the *Bulletin of Entomological Research* (December 1940) is "A Physiological Study of Mosquito Larvæ which were Treated with Anti-Malarial Oils." It is an extract from my M.D. Thesis read at Cambridge in February 1940. In it I have recorded results and conclusions reached after hours and sometimes days of studying individual larvæ before, during, and after they were treated with a variety of oils. I saw larvæ suffocated, poisoned, starved to death with their feeding-brushes matted by oil. I saw them drown after only external contact with oil droplets, or starve when their food supply of micro-organisms was killed, though the larvæ were unharmed by oil. I saw some oils flow easily into the larvæ's tracheæ, and other oils actively drawn into the tracheæ with a meniscus convex towards the air in the lumen. These oils killed the larvæ, but they would never last for days as a permanent film over a stream.

I saw young larvæ get some toxic oil on to their feeding-brushes or their external cuticle and die, though no oil obstructed their tracheæ; yet I saw other young larvæ, with some non-toxic oil in one trachea only, moult their skins to survive, pupate and hatch. Therefore when I read that "Pupation is prevented when oil penetrates larval tracheæ; it is therefore most desirable to produce a permanent film on water," then I wonder whether the writer, or the reader who agrees, has any conception of what is really done when malaria is controlled by oiling a tropical stream.

In the paragraph headed "Maintainance of Stable Films" there is an example of that "erroneous conclusion" against which Dr. Lord warns us. He describes a certain oil with an "excellent initial spread on water"—a property he assumes is of no value to a sanitarian cleaning up an unhealthy stream. He complains of the oil film breaking up after about 5 minutes, and then describes the appearances after 10–12 hours. Does he stop to think how many of the larvæ which "thrived for at least 24 hours" had already got oil into both tracheæ? When he talks of "true toxicity" is he misled by his so-called toxicity tests "obtained in the usual way" into thinking that a larva is necessarily dead because it is forced below the surface for 15 minutes or even 1½ hours? Does he think that, because a larva remains alive for 24 hours or even longer, it has not enough oil in its tracheæ to prevent development? Does he realize that the choice of an anti-malarial oil is almost solved without more ado in a locality, if there exists here a cheap oil with a high degree of initial spread, toxic enough to kill a larva before it next moults its skin? If Dr. Lord agreed with this, he would not have written that "the oil in question is not at all suitable for anti-malarial work."

Dr. Lord sets out the characteristics of anti-malarial oils. And he adds: "It may be stated at once that the original Malariol passed the above criteria fairly satisfactorily. . . . Moreover, according to Murray's work, its constitution was quite wrong, since it contained 50 per cent. of aromatics of a boiling range similar to the non-aromatics." One is inclined to make an appeal to all who would engage in the study of anti-malarial oils to pause. Let them consider not only the physical and chemical properties of oil spreading on very clean water in dishes, in which laboratory larvæ lazily swim. Let them think occasionally of that dynamic struggle for existence, fought out by hungry larvæ in a tropical stream. Let them imagine, from the larva's point of view, what are the many physiological perils to be feared apart from that laboratory ideal—the Permanent Film. Dr. Lord's observations on the physical and chemical properties of blends containing P.D. residue are of real value. His information on other aspects of anti-malarial oiling is limited for want of a wider outlook.

DR. T. H. BISHOP (*Medical Adviser, Iraq Petroleum Co., Ltd.*) writes:

The subject of Dr. Lord's paper is one of considerable importance to all interested in malariology *per se*, and also to those concerned, either as employers or administrators, with the public health in tropical and sub-tropical climates. The appreciable improvement which he records as having been obtained in the spreading pressure of the Burmah Oil Company's product, Malariol, is a noteworthy advance, and although it be granted

that the product has a commercial value, it is a matter for congratulation that a commercial firm is willing to undertake such a research—the chief object of which is to improve the technical equipment of the tropical sanitarian.

Dr. Lord is right in stating that much medical research has been done on the subject of malaria, but anyone who has spent years of service in such malarial-ridden tracts as Bengal and the United Provinces of India will question his suggestion that the disease is more terrible to those who have not experienced it than to those *e.g.* who, having contracted it in infancy, have never been free of its debilitating and devitalizing effects throughout their shortened lives. To them and to those responsible for the public health in these Provinces, as it must be elsewhere, the disease is a curse as relentless as it is terrible, for the million odd deaths which is India's annual malarial mortality toll is, as Dr. Lord again points out, only a part—and experience suggests a relatively small part—of the total morbidity due to this mosquito-borne infection.

The story of malaria is a cogent reminder not only of the exasperating hindrances and occasional hectic successes besetting human effort, but also of the *ars longa vita brevis* which must qualify the optimism of early success. In an enthusiastic account of the magnificent anti-malarial work done by Colonel Gorgas and his staff in the Panama Canal zone, Sir Ray Lankester was moved to declare that such men "have not merely done a piece of sanitary cleaning up, they have first imagined and then created by the force of human will, directed and maintained by the conviction of the reality of science, a new thing—the tropics without deadly fever." This was written more than thirty years ago, when the thorough and painstaking effort of Gorgas had not only brought success where de Lesseps failed, but had also registered the most noteworthy triumph for Ross's discovery of the rôle of the mosquito in malaria transmission. Other striking successes followed in Malaya and Africa, and continue to-day in urban districts and similarly closely supervised areas, such as tea estates, oil and mining concessions, and railway colonies in the East. But whether the happy prospect envisaged by Sir Ray Lankester is any nearer realization to-day than when he wrote of it is a matter concerning which a study of recent malaria statistics makes one dubious, for side by side with the hopeful mortality returns of urban areas are to be seen the depressing figures for rural areas which, in India, consist mainly of villages built round insanitary "tanks" enveloped by jungle and isolated from one another by extensive tracts of undrained, often submerged agricultural land. A comparatively recent record for Bengal and the United Provinces illustrates :—

| Province. | No. of deaths from malaria. | Rate per mille. |
|---|---|---|
| Bengal : | | |
| Urban areas . . . . . | 2,090 | 0·8 |
| Rural areas . . . . . | 346,121 | 7·5 |
| United Provinces : | | |
| Urban areas . . . . . | 21,800 | 5·8 |
| Rural areas . . . . . | 910,996 | 20·4 |

Such a gross disparity suggests that prophylactic measures must either be largely disregarded or singularly ineffective in rural areas. But disparity in the degree of success attending anti-malarial measures goes farther than this, and the very name "malaria" perpetuates our ignorance of the many factors which go to prove that, in malariology, sauce for the goose is by no means invariably an appropriate sauce for the gander, and that such phenomena as sunlight and shade, humidity and temperature, the presence or absence of certain vegetation, and the degree of salinity are determinants in the intensification or diminution of malarial morbidity, so we still seem to be far from that panacea which is to realize Sir Ray Lankester's dream, and it is even doubtful whether, despite brilliant successes, the world incidence of malaria has decreased to any appreciable extent since Ross's discovery. Ignorance is, doubtless, largely responsible for this in many malarial-ridden countries, but what Colonel Sinton terms "man-made malaria"—*i.e.*, the creation of malaria-fostering conditions not only by private individuals and communities, but even by Governmental and local administrators—is still so considerable a factor in India, the pioneer home of malarial research, that it may well outweigh the successes of enlightened sanitarians.

It cannot be said that workers have not been prolific of inhibitory devices, for the latter vary from mosquito-repellent skin applications and mosquito-proofing to large-scale systems of drainage, but for urban districts and similar restricted and supervised areas the usefulness of appropriate larvicides is universally admitted. The variety of these is great, and it is to be expected that some are found to be more potent in destruction than others. Sir Malcolm Watson, in his address at last year's annual meeting of the Ross Institute, spoke of an anti-malarial mixture which he used in 1914 and thought "might almost be called the perfect anti-malarial mixture." This, he claimed, "saved thousands and an incalculable amount of money for estates. It killed all larvæ in running streams, and it killed adult mosquitoes which came to lay their eggs in pools at the side of the streams, because it trapped them. It killed grass and vegetation on the sides of the streams. It killed surface-floating algæ; it made other profound changes in the stream, so that a particular alga grew at the bottomof the stream, and where that occurred we never had been able to find dangerous species of anopheles. We had altered the minute vegetable life in the stream and made it unsuitable for mosquitoes to live in it. That," concluded Sir Malcolm, "was very satisfactory, and had it been known at the time it would have been a great advantage in Salonika. One of the reasons for the big epidemic there was that they did not have the right kind of anti-malarial oil." Surely scarcely anything more could be expected of any larvicide, and although it may be that the mixture in question was a local product peculiarly well-suited to local conditions, one can imagine that all practical chemists interested in larvicides would be grateful for Sir Malcolm's formula.

There are many theories as to the way in which mosquito larvæ are destroyed by a surface oil film: suffocation, blocking of the respiratory tubes, toxic effects, and, most ingenious of all, drowning as a result of the reduction of surface tension which makes it impossible for the larva to "hang on" at the surface and secure the requisite amount of air.

That there must be oxygen deprivation is obvious, but Dr. Lord's tests for toxicity, which are confirmed by the results obtained with such toxic substances as Paris green, copper sulphate, and cresol, suggest that the toxic effect of the oil film is also a potent factor. The adult mosquito's vulnerability to such deterrents as carbon tetrachloride, methyl salicylate, naphthaline, and pyrethrum, when used with kerosine oil in sprays is still further confirmation of the value of toxic agents and would seem to point to the possibility of a wider use for such in the treatment of large tracts of larvæ-infected water. Having regard to the great preponderance of "rural" over "urban" malaria, this seems a problem which the practical chemist might find well worthy of attention.

Accumulating knowledge of the habits and hazards of mosquito larvæ indicates how great is the variety of optimal breeding conditions. For example, the chief malaria-carrier in Assam and the Bengal Dooars (*Anopheles Minimus*) neither grows at the edge of streams or pools nor thrives in shade, and can therefore be discouraged, as proved by Dr. Ramsay, by the growing of shade-producing vegetation, while other varieties thrive best in contrasted conditions: at the grassy edges of swift running streams (*Aconitus Dönitz*); in shaded pools along forest streams (*Aitkini James*); in tree holes (*Annandalei, Barianensis*, and others); in collections of muddy water (*Subpictus*); in weedy and rain-water pools (*Pulcherrimus*); in hill streams at altitudes of 4000 to 8000 feet (*Gigas* and *Lindesayi*), and so on. Again, as already noted, it has been proved that temperature and humidity may favour or retard mosquito multiplication, while the concentration of salts, either too great or too small, may form a limiting factor in larval development. That Nature has provided such varying conditions for the business of mosquito propagation suggests that in the production of a successful larvicide both chemist and sanitarian should find very ample scope for their combined scientific inquisitiveness.

DR. LORD in reply to the Discussion wrote:—

The conditions in Iran described by Dr. Young—namely, "dry heat at one time, humidity at another"—are similar to those in many parts of India and Burma. Whilst, therefore, the ultimate test of any anti-malarial oil must be a practical trial, it is felt that with its relatively low volatility and other good properties Malariol should prove effective in the Iranian fields.

With regard to volatility, it is of interest to note that during the hottest and driest spells, the necessity for spraying is less than in cooler but more humid periods, when breeding is more prolific.

Whilst appreciating the force of the view that stagnant water "should be rendered unfit for larvæ to breed in, regardless of other considerations, such as vegetable or animal life," nevertheless, it must be pointed out that some users stipulate that an anti-malarial oil should be non-injurious to animals, etc., and in any case if the oil possesses these advantages it is all to the good.

Professor Adam mentions a simple and cheaper apparatus than that used at Syriam, which should be quite suitable and accurate enough for research work or routine testing of anti-malarial oils. He also outlines rough tests which should prove of considerable value in the field.

Lieut. Watson, M.D., appears to be somewhat "stream-minded." It is wished to stress here, however, that an anti-malarial oil should be effective in dealing with *either* stagnant water *or* streams, and it is claimed that an oil possessing the good qualities enumerated in the paper is suitable for both purposes. Lieut. Watson rather scorns the idea of stable films of oil, and indicates that a toxic product with a high degree of initial spread is all that is required. But it will surely be obvious to almost every reader that a continuous film, stable for several days, is bound to be more effective on stagnant water than an oil, which spreads well initially and then quickly collects into lenses; and a little thought will soon show that the former oil will also be more effective on running water. An oil with a good initial spread, but no stable film, will kill larvæ which come in contact with it when it is first sprayed on a stream—but its effect will be short-lived—whereas the oil which spreads just as well initially, and produces a stable film, will creep in part to the side of the stream (often congested with weeds), where the water is almost if not quite stationary, and remain effective for days, whilst the portion which flows down the stream will still be in the form of a film, and therefore much more effective than the oils which Lieut. Watson regards as satisfactory.

It is strange to find the author accused of a limited outlook, and a lack of appreciation of the physiological problem of how most cheaply to rid a flowing stream of anopheline larvæ, by someone who makes the somewhat ingenious statement that various oils "kill mosquitoes and their larvæ, not because of this or that fraction in their formula, but because mosquitoes were not built to live in oil." He also asks if the author "realizes that the choice of an anti-malarial oil is almost solved without more ado in a locality, if there exists here a cheap oil with a high degree of initial spread, toxic enough to kill a larva before it next moults its skin?" Lieut. Watson seems to have missed the main purpose of the paper, which was to discuss the fundamental principles involved, and then describe the necessary attributes of a good, cheap anti-malarial oil, so that consumers would not in future make faulty choices of the type indicated by him.

With regard to the other queries raised, it may be stated, in the first place, that a full description of the toxicity test is given in the paper. Secondly, if toxicity tests are carried out on two oils *A* and *B*, and in the case of oil *A* all the larvæ are "down" in 10–11 minutes, whereas with oil *B* some are very active after 24 hours, the supremacy of *A* is so great that the question as to whether those remaining alive after 24 hours in case *B*, develop fully later, or contain oil in both tracheæ, is only of minor importance. In point of fact many did develop into mosquitoes, but insufficient tests were carried out to fix the percentage accurately. Thirdly, the author has not been "misled into thinking that a larva is necessarily dead because it is forced below the surface for 15 minutes or even for one and a half hours," but he does know that when larvæ described as "down" in the paper have been removed to clear running water, they have never developed into mosquitoes.

Dr. Bishop rightly stresses the great variety of optimal breeding conditions for different mosquitoes, and the enhanced difficulties thereby introduced in trying to eliminate the disease. But he is, perhaps, a little too pessimistic. There can be no doubt that many large tracts of land, previously ridden with malaria, are now almost if not quite malaria-free, and this is surely an indication that still further rewards will be the result of continued effort. The author agrees that all interested in larvicides would be grateful for Sir Malcolm Watson's formula for the product, which he stated "might almost be called the perfect anti-malarial mixture."

The Honorary Editor will be pleased to receive further contributions to the Discussion on Dr. Lord's paper for subsequent publication in the *Journal*.

# THE INVESTIGATION OF HIGH-BOILING PETROLEUM OILS BY ADSORPTION ANALYSIS.

By B. C. Allibone.

Summary.

This paper describes the application of " chromatographic adsorption " to the analytical separation of the high-boiling components of petroleum. A distillation cut of restricted boiling range is dissolved in aromatic free petroleum ether, b. pt. 60–80° C., and the solution filtered through a column of adsorbent. The adsorbent may advantageously be silica gel. After the addition and exhaustion of the primary solution, fresh petroleum ether is added to the top of the column and the filtration continued until the high-boiling material recovered from a unit of filtrate approaches a specific gravity of unity. The adsorbent is then drained by suction, removed from the column, and allowed to dry. The dried adsorbent is divided into suitable portions as its variation in colour or other consideration may dictate, and extracted with a solvent or a succession of solvents. By these means, with variations to suit individual stocks, high-boiling cuts, whether distillates or residues, may be separated into a succession of components of widely varying physical characteristics.

The application of the procedure and the degree of separation achieved are illustrated by means of selected examples.

The composition of lubricating oils and the properties of the components have in the main been studied by a separation into groups of varying hydrogen content. Extensive investigation on these lines was carried out by Mabery,[1] who separated the lubricating fractions of five typical crude oils by means of fractional solution using ether alcohol. Subsequently Wilson and Allibone [2] resolved the lubricating constituents of Burma and Hardstoft crudes into fractions of progressively varying hydrogen content by the use of acetone–$SO_2$. The advent of solvent refining of lubricating stocks as a common refinery operation and the analogies drawn between this art and that of fractional distillation by Saal and Van Dyck [3] led to an improved application of solvents to the separation of lubricating-oil components, with the result that the sharpness of separation was much improved. Investigation has been conducted by a number of workers, but the results obtained by Cannon and Fenske [4] may be taken as typical. These workers separated a dewaxed distillate from Van Zandt crude into a large number of fractions by a procedure which included the use of a reflux extraction unit in which acetone was used as the solvent. A drastic segregation of the charging stock into components of varying boiling point and viscosity index was achieved, the latter property covering a range of −114 to 109. The authors pointed out that although the oil fractions charged to the reflux apparatus represented but 0·05 per cent. of the original crude, no appreciable quantity of intermediate viscosity-index material between 10 to 90 was obtained, the transition from the negative to the highly positive viscosity index region being very sharp. The present communication directs attention to the existence of an alternative procedure for a similar segregation, that of adsorption analysis, and illustrates the use of the method by means of selected examples.

The phenomenon of adsorption is no stranger to the petroleum world, for its utilization in the refining of mineral oils is a standard practice, and the assessment of the effects of percolation or batch treatment in the improvement of product quantity is a well-known operation in petroleum laboratories. In an analytical sense, however, its employment is not so common, although Garner some years ago, using animal charcoal, applied the procedure to the estimation of resins in lubricating oil.[5] Since that time there have been sporadic reports of its application to petroleum products, and *inter alia* the segregation of aromatic compounds and of paraffins have been described. Thus Mair and co-workers have described the separation of low-boiling petroleum hydrocarbons with silica gel [6] and the use of silica gel in their exhaustive fractionation of a lubricant fraction of Oklahoma petroleum.[7]

Further, Willingham [8] has noted that from solutions of hydrocarbons of high molecular weight, silica gel selectively adsorbs aromatic hydrocarbons in preference to naphthenes and paraffins. Using binary mixtures consisting of 20 per cent. of aromatic in 20–25 gm. of paraffin hydrocarbon, the mixture being filtered through 20 gm. of gel, a separation, for example, of 1-*p*-diphenyloctadecane, $C_6H_5.C_6H_4C_{18}H_{37}$, from *n*-dotriacontane, $CH_3(CH_2)_{30}CH_3$, was achieved. In that particular experiment 3·3 gm. of the aromatic hydrocarbons were held by the gel.

The author's attention to the broader possibilities of adsorption had, however, been attracted by earlier workers, especially by the contribution of Winterstein and Schön published in the *Zeit. für physiologische Chemie* of 1934,[9] reporting the successful separation by preferential adsorption of certain aromatic hydrocarbons—for example, anthracene and naphthalene. A typical experiment consisted of the filtration of 50 mgm. of anthracene plus 150 mgm. of naphthalene in 200 ml. of petroleum ether through 150 gm. of aluminium oxide—*i.e.* 750 gm. of adsorbent per gram of hydrocarbon solute. The anthracene was left behind in the upper half of the column.

The experiment just described is an example of the general procedure known as chromatographic adsorption, a method first brought to notice by Twsett,[10] and consisting in essence of the separation of mixtures, especially of coloured components, from their solutions by means of suitable solid adsorbents. The method has received widespread application in the separation of organic colouring matters such as carotin, chlorophyll, etc.

The quantities of adsorption agent used are normally high; thus for

1 gm. of carotin, 2000 gm. of clay are required;
1 gm. of lutein, 5000 gm. of aluminium oxide;
1 gm. of chlorophyll, 1000 gm. of sugar.[11]

An exhaustive account of the published information has been given by Zechmeister in his compilation "Die chromatographische adsorptions methode."

Although Zechmeister barely mentions the use of silica gel, the ability of this material to adsorb aromatic hydrocarbons preferentially had been known some years before the prior publication of Tarasov in 1927 noted by Mair and White,[6] and therefore in an adaptation of the technique to the

investigations of petroleum this adsorbent automatically became first choice for trial.

In accordance with anticipation, silica gel was found very suitable for the present purpose, although bauxite, and presumably other forms of aluminium oxide, are almost as effective for residua. Silica gel is suitable, however, for the complete range, gas oil to crude-oil residues.

## Experimental Procedure.

Typical experimental conditions are represented by 50 gm. of charge of restricted boiling range dissolved in 500 ml. of aromatic free petroleum ether. The solution is filtered at room temperature through 300 gm. of silica gel in a column of length/diameter ratio of, say, 15/1. 100-ml. fractions of filtrate are collected and fresh petroleum ether is added as necessary to the top of the column of gel. Each filtrate fraction is stripped of solvent in a stream of carbon dioxide, with or without the application of vacuum, as expediency may dictate. After collecting a suitable number of fractions, determined by the character and quantity of the later stripped fractions, the column of gel is drained under suction and the washings are added to the last filtrate fraction. The drained gel is then removed from the tube, divided into convenient portions—as variation in colour of the gel or other consideration may suggest—and after allowing to dry, is extracted in a Soxhlet apparatus with methyl ethyl ketone, this having been found to be the most efficacious of the common solvents. The gel is subsequently recovered by roasting.

An unrefined distillation residue from a dewaxed distillate cut was examined by the above simple procedure. The characteristics of the charging stock were :—

| | |
|---|---|
| Sp. gr. at 60° F. . . . . | 0·927 |
| Viscosity, Redwood, at 140° F. . . . | 298 |
| Setting point, °F. . . . . | 18 |
| 100 mm. distillation test— | |
| I.B.P., °C. . . . . | 287 |
| 50% at. . . . . | 305 |
| F.B.P. . . . . | 331 |

This yielded the data given in Table I on the following page.

By combination of Fractions 1–5, 6–9, and 10–12 inclusive the resolution of the charge may be expressed as :—

| | | |
|---|---|---|
| 59·65 | per cent. by volume | of low-gravity oil of sp. gr. 0·875 |
| 15·45 | ,, ,, | intermediate gravity oil of sp. gr. 0·927 |
| 24·90 | ,, ,, | solid resin of sp. gr. 1·059. |

Whilst the separation is imperfect and could be improved by re-running of selected fractions, the results as obtained represent a more complete evaluation than is customary, and the attractiveness of the method is not lessened by the fact that such an assessment may be made in a couple of working days.

TABLE I.

*Examination of an Unrefined Residue ex Dewaxed Pressable Wax Distillate.*

(Treatment quantities as per text.)

| Fraction No. | Vol. No. | Recovered component of charge. | | | | Cumulative recovery. | | |
|---|---|---|---|---|---|---|---|---|
| | | Gm. | Per cent. by wt. | Per cent. by vol. | Sp. gr. at 60° F. | Per cent. by vol. | Sp. gr. at 60° F. | |
| 1 | 100 | 6·38 | 12·74 | 13·65 | 0·867 | 13·65 | — | Fractions 1–5, per cent. by vol. 59·65. |
| 2 | ,, | 5·25 | 10·48 | 11·10 | 0·875 | 24·75 | — | |
| 3 | ,, | 5·40 | 10·77 | 11·45 | 0·875 | 36·20 | — | Sp. gr. at 60° F., 0·875. |
| 4 | ,, | 5·40 | 10·77 | 11·40 | 0·876 | 47·60 | — | Visc., Redwood, 140° F., 145. |
| 5 | ,, | 5·72 | 11·41 | 12·05 | 0·878 | 59·65 | — | V.G.C., 0·795.<br>V.I., 97.<br>Colour, white.<br>Set point, 32° F. |
| 6 | ,, | 2·56 | 5·11 | 5·25 | 0·903 | 64·90 | — | Fractions 6–9 inclusive, % by vol. 15·45. |
| 7 | ,, | 1·46 | 2·91 | 2·95 | 0·914 | 67·85 | — | Sp. gr. at 60° F., 0·927. |
| 8 | ,, | 1·45 | 2·89 | 2·90 | 0·932 | 70·75 | — | Somewhat sticky. |
| 9 | 195 | 2·25 | 4·50 | 4·35 | 0·961 | 75·10 | — | Very viscous, sticky, almost colourless. |
| 10 | M.E.K. extract | 3·17 | 6·33 | 5·85 | 1·007 | 80·95 | — | Very soft resin, green bloom. |
| 11 | ,, | 3·98 | 7·94 | 7·00 | 1·052 | 87·95 | — | Hard red resin. |
| 12 | ,, | 7·09 | 14·15 | 12·05 | 1·089 | 100·00 | 0·928 | Dark brittle resin. |
| | | 50·11 | 100·00 | 100·00 | | | | |

## FACTORS INFLUENCING THE EFFICACY OF THE METHOD.

In addition to the nature of the charging stock, factors influencing the efficacy and scope of the method include :—

(1) the proportion of adsorbent used;
(2) the fractional sub-division of the filtrate;
(3) the concentration of the charge in the petroleum ether diluent.

The ratio used in the example cited—viz., 6 gm. of gel per gram of charge—has proved suitable for most charging stocks. In these circumstances the addition of the whole charge usually results in coloration of about half the gel column. With the subsequent addition of pure solvent, washing out occurs, and colour gradually spreads to the bottom of the column until coloured components emerge in the filtrate. This reversibility of the adsorption, coupled with the impossibility under the given conditions of applying the whole of the charge at one and the same time, is prejudicial to good separation, but these adverse influences may be countered, if desired, by increasing the proportion of gel in some degree towards the limiting conditions existent when the amount of gel wetted by the application of the charge solution is an infinitely small proportion of the whole gel. Alternatively, re-running of selected fractions may be employed.

Then, unless the fractions be sufficiently small, it will be impossible to take advantage of the degree of separation inherent to the gel/oil ratio adopted. This subdivision will be normally governed by the size of oil fraction required for subsequent examination, and hence semi-micro methods of examination, such as capillary pyknometers for the determination of specific gravity, facilitate the application of the method.

As regards the concentration of charging stock in the petroleum-ether

carrier, the dilution employed—about 10/1—has been found generally useful. It may be reduced considerably, to as low as about 2/1, without affecting the results to a marked extent, but such a reduction of dilution tends to give large proportions of charge in the initial filtrate, and is particularly disadvantageous in re-running operations. Usually separation is required in reasonable sub-division, say 5 or 10 per cent. fractions at a convenient time-interval, and with a high charge/solvent ratio it is more difficult to ensure that this shall occur.

### Application to Special Charging Stocks.

Operational variants are required for special stocks. In the case of stocks containing wax or asphaltic matter in excess of the solvent capacity of the solvent, this excess is preferably removed before filtration. In the case of wax-bearing stocks, whether requiring pre-removal of wax or not, it is convenient to bulk selected filtrate fractions for dewaxing and afterwards to separate the lubricant components by re-running. Alternatively, a stock may be dewaxed prior to adsorption analysis, but the precise procedure to be adopted will depend on the requirements of the individual case. Residual stocks vary from non-resinous to the highly asphaltic. The latter occasion some difficulty, in that not only do they yield a substantial precipitate of hard asphalt in making up the primary solution in petroleum ether, but this separation, being but a single equilibrium, is imperfect. The gel does not readily adsorb the asphalt compounds left in solution, and quickly becomes exhausted when such solutions are filtered. It is preferable to clean up the solution or the original stock before attempting filtration. As for waxy stocks, the procedure to be employed varies from case to case. Thus a residual stock yielding 6·9 per cent. of hard asphalt on first solution was subsequently filtered through the gel without intermediate treatment, but another stock giving 19 per cent. of hard asphalt required to be treated prior to filtration. For convenience such treatment may be by acid and clay, although if recovery of all constituents without change is desired, treatment with liquid propane is to be preferred.

The accuracy of the operation may be checked by a weight balance, which in general will be within $\pm$ 0·5 per cent., and frequently very much closer.

The specific cases which follow serve to illustrate the scope of the method, and include data secured from the treatment of pressable wax distillates, residual stocks, and commercial grades of Penna and Western bright stock.

### The Analysis of Pressable Wax Distillate.

Pressable wax distillates usually contain components boiling between 150° and 300° C. at 10 mm. Hg pressure, and individual component cuts may vary from gas oil to a heavy lubricating oil. Since the retentivity of the gel for a compound of a given chemical class increases with the molecular size of the compound, so that a compound of high boiling point is held more firmly in the gel than is a related compound of lower boiling point, it is preferable to submit the wax distillate either before or after dewaxing to a fractional distillation into five or more closely cut fractions.

A typical instance is represented by a dewaxed pressable wax distillate as follows :—

TABLE II.

*Dewaxed Wax Distillate.*

(Sp. gr. at 60° F., 0·928.)

| Fraction : | 1. | 2. | 3. | 4. | 5. |
|---|---|---|---|---|---|
| Per cent. by vol. of charge . | 19·8 | 19·7 | 19·8 | 18·9 | 21·8 |
| Sp. gr. at 60° F. . . . | 0·871 | 0·898 | 0·922 | 0·942 | 0·956 |
| 10 mm. distillation— | | | | | |
| I.B.P., ° C. . . . | 110 | 180 | 209 | 240 | 277 |
| 10% over . . . . | 137 | 184·5 | 214 | 246 | 285 |
| 50% ,, . . . . | 157 | 189·5 | 220 | 252 | 294 |
| 90% ,, . . . . | 170 | 200 | 229 | 261 | 317 |
| F.B.P., ° C. . . . | 175 | 203 | 233 | 266 | 331 |

These five fractions, on processing in the manner of Table I, yielded data which are reproduced in Table III below :—

TABLE III.

*Details of the Adsorption Analysis of Fractions from Dewaxed Pressable Wax Distillate.*

| Fraction No. | Filtrate, ml. | Per cent. by vol. of charge. | | Specific gravity at 60° F. | |
|---|---|---|---|---|---|
| | | Fraction. | Cumulative. | Fraction. | Cumulative. |
| | *Fraction* 1.—19·8% by vol. of charge. Sp. gr. at 60° F., 0·868. Viscosity at 140° F., *ca.* 34. | | | | |
| 1 | 100 | 14·2 | 14·2 | 0·813 | 0·813 |
| 2 | ,, | 13·0 | 27·2 | 0·824 | 0·817 |
| 3 | ,, | 13·85 | 41·05 | 0·822 | 0·819 |
| 4 | ,, | 13·4 | 54·45 | 0·823 | 0·819 |
| 5 | ,, | 13·2 | 67·65 | 0·825 | 0·821 |
| 6 | ,, | 4·95 | 72·6 | 0·868 | 0·825 |
| 7 | ,, | 3·4 | 76·0 | 0·941 | 0·830 |
| 8 | ,, | 4·2 | 80·2 | 0·955 | 0·837 |
| 9 | 240, including drainage | 8·15 | 88·35 | 0·981 | 0·850 |
| 10 | M.E.K. extract | 8·65 | 97·0 | 1·023 | 0·864 |
| 11 | ,, | 3·0 | 100·0 | 1·031 | 0·870 |
| | *Fraction* 2.—19·7% by vol. of charge. Sp. gr. at 60° F., 0·895. Viscosity at 140° F., *ca.* 39. | | | | |
| 1 | 100 | 13·2 | 13·2 | 0·825 | 0·825 |
| 2 | ,, | 11·5 | 24·7 | 0·836 | 0·832 |
| 3 | ,, | 11·8 | 36·5 | 0·835 | 0·833 |
| 4 | ,, | 12·0 | 48·5 | 0·837 | 0·834 |
| 5 | ,, | 12·7 | 61·2 | 0·836 | 0·834 |
| 6 | ,, | 4·75 | 65·95 | 0·877 | 0·837 |
| 7 | ,, | 3·6 | 69·55 | 0·931 | 0·840 |
| 8 | ,, | 4·3 | 73·85 | 0·967 | 0·849 |
| 9 | 240 | 8·55 | 82·4 | 0·993 | 0·864 |
| 10 | M.E.K. extract | 8·25 | 90·65 | 1·035 | 0·877 |
| 11 | ,, | 5·95 | 96·6 | 1·057 | 0·890 |
| 12 | ,, | 3·4 | 100·0 | 1·047 | 0·896 |

TABLE III—*continued.*

| Fraction No. | Filtrate, ml. | Per cent. by vol. of charge. | | Specific gravity at 60° F. | |
|---|---|---|---|---|---|
| | | Fraction. | Cumulative. | Fraction. | Cumulative. |
| | *Fraction* 3.—19·8% by vol. of charge. Sp. gr. at 60° F., 0·920. Viscosity at 140° F., *ca.* 53. | | | | |
| 1 | 100 | 11·5 | 11·5 | 0·835 | — |
| 2 | ,, | 10·6 | 22·1 | 0·845 | — |
| 3 | ,, | 10·6 | 32·7 | 0·846 | — |
| 4 | ,, | 10·8 | 43·5 | 0·846 | — |
| 5 | ,, | 11·35 | 54·85 | 0·848 | 0·845 |
| 6 | ,, | 5·25 | 60·1 | 0·901 | |
| 7 | ,, | 4·85 | 64·95 | 0·923 | |
| 8 | ,, | 4·6 | 69·55 | 0·978 | |
| 9 | 300 | 10·1 | 79·65 | 1·009 | |
| 10 | M.E.K. extract | 7·85 | 87·5 | 1·030 | |
| 11 | ,, | 6·55 | 94·05 | 1·055 | |
| 12 | ,, | 5·95 | 100·0 | 1·072 | 0·916 |
| | *Fraction* 4.—18·9% by vol. of charge. Sp. gr. at 60° F., 0·938. Viscosity at 140° F., 125. | | | | |
| 1 | 100 | 12·4 | 12·4 | 0·854 | 0·854 |
| 2 | ,, | 10·0 | 22·4 | 0·869 | 0·862 |
| 3 | ,, | 10·1 | 32·5 | 0·869 | 0·865 |
| 4 | ,, | 10·4 | 42·9 | 0·869 | 0·865 |
| 5 | ,, | 8·75 | 51·65 | 0·877 | 0·865 |
| 6 | ,, | 1·45 | 53·1 | 0·921 | 0·869 |
| 7 | 200 | 4·9 | 58·0 | 0·896 | 0·870 |
| 8 | 300 | 8·15 | 66·15 | 0·957 | 0·881 |
| 9 | 400 | 6·85 | 74·0 | 1·005 | 0·895 |
| 10 | 890 | 7·6 | 80·6 | 1·037 | 0·907 |
| 11 | M.E.K. extract | 8·3 | 88·9 | 1·064 | 0·921 |
| 12 | ,, | 11·1 | 100·0 | 1·077 | 0·939 |
| | *Fraction* 5.—21·8% by vol. of charge. Sp. gr. at 60° F., 0·956. Viscosity at 140° F., 519. | | | | |
| 1 | 100 | 10·4 | 10·4 | 0·856 | 0·869 |
| 2 | ,, | 9·2 | 19·6 | 0·872 | 0·869 |
| 3 | ,, | 9·0 | 28·6 | 0·876 | 0·872 |
| 4 | ,, | 9·2 | 37·8 | 0·877 | 0·873 |
| 5 | ,, | 9·4 | 47·2 | 0·879 | 0·874 |
| 6 | ,, | 4·5 | 51·7 | 0·917 | 0·876 |
| 7 | ,, | 4·0 | 55·7 | 0·918 | 0·880 |
| 8 | ,, | 3·2 | 58·9 | 0·948 | 0·884 |
| 9 | 287 | 7·5 | 66·4 | 0·999 | 0·897 |
| 10 | M.E.K. extract | 9·1 | 75·5 | 1·039 | 0·915 |
| 11 | ,, | 10·4 | 85·9 | 1·063 | 0·932 |
| 12 | ,, | 14·1 | 100·0 | 1·097 | 0·955 |

As may be seen by inspection, the general resolution was similar to that noted in Table I, yielding initially fractions of low specific gravity, next smaller fractions of higher gravity, finishing with cuts of high specific gravity.

By bulking the three types an outline resolution is achieved as in Table IV.

TABLE IV.

*Outline Results from the Resolution of Fractions of Dewaxed Pressable Wax Distillate.*

| No. | Main fraction. | | Light cut. | | Intermediate cut. | | Heavy cut. | | |
|---|---|---|---|---|---|---|---|---|---|
| | Vol. % of charge. | Sp. gr. at 60° F. | Per cent. by vol. | Sp. gr. at 60° F. | Per cent. by vol. | Sp. gr. at 60° F. | Per cent. by vol. | Sp. gr. at 60° F. | Character. |
| 1 | 19·8 | 0·868 | 67·65 | 0·821 | 12·55 | 0·917 | 19·80 | 1·008 | Brown fluid, not sticky. |
| 2 | 19·7 | 0·895 | 61·20 | 0·834 | 12·65 | 0·921 | 26·15 | 1·030 | ,, ,, ,, |
| 3 | 19·8 | 0·920 | 54·85 | 0·845 | 14·70 | 0·932 | 30·45 | 1·037 | Oily, not sticky. |
| 4 | 18·9 | 0·938 | 51·65 | 0·865 | 14·50 | 0·930 | 33·85 | 1·050 | Soft resin. |
| 5 | 21·8 | 0·956 | 47·20 | 0·874 | 11·70 | 0·945 | 41·10 | 1·058 | Hard resin. |

As the filtrations were carried out in a uniform manner, and as the volumes of the five filtrate fractions and the properties of the oils do not show anomalies either of quantity or properties, it is certain that the five cuts numbered are chemically similar, and that the progressive diminution in percentage shown in the table, of these, the most highly saturated, hydrocarbons, is genuine.

TABLE V.

*Re-running of Selected Bulked Fractions Secured from Fraction 5 of Dewaxed Pressable Wax Distillate.*

*Fraction 5.—100% Sp. gr. 0·921*

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| 6·10% | Sp. gr. 0·857 | 4·50% | Sp. gr. 0·875 | 4·20% | Sp. gr. 0·892 | 1·45% | Sp. gr. 0·981 | | |
| | | 28·10% | ,, 0·877 | 2·15% | ,, 0·919 | | | | |
| | | 5·00% | ,, 0·877 | 7·10% | ,, 0·930 | | | | |
| | | | | 1·60% | ,, 0·966 | 1·35% | Sp. gr. 0·992 | | |
| | | 37·60% | ,, 0·877 | | | 4·40% | ,, 1·008 | | |
| | | | | 15·05% | ,, 0·921 | 27·05% | ,, 1·058 | | |
| | | | | | | 7·00% | ,, 1·095 | | |
| | | | | | | 39·80% | ,, 1·057 | | |
| | | | Re-run | | | | Re-run | | |
| 35·35% | 11·25% | Sp. gr. 0·852 | | 1·05% | Sp. gr. 0·879 | | | | |
| | 9·10% | ,, 0·873 | | 0·95% | ,, 0·910 | | | | |
| | 9·05% | ,, 0·876 | | 1·30% | ,, 0·903 | | | | |
| | 5·95% | ,, 0·897 | | 2·45% | ,, 0·898 | | | | |
| | 0·80% | ,, 0·893 | | 2·40% | ,, 0·908 | | | | |
| | 1·25% | ,, 0·969 | | 1·95% | ,, 0·916 | | | | |
| | 0·20% | ,, 0·980 | Assumed | 1·90% | ,, 0·927 | | | | |
| | | | | 2·55% | ,, 0·959 | | | | |
| | 37·60% | ,, 0·876 | | 0·50% | ,, 0·978 | | | | |
| | | | | 15·05% | ,, 0·919 | | | | |

Corresponding to this progressive diminution, there is a progressive increase in content of compounds having specific gravity greater than unity. These vary in nature from mobile fluids to hard resins, depending on the fraction from which they are derived. In addition, there are middle cuts of slightly irregular quantity, which are in the main composed of compounds belonging to the low- and high-gravity cuts on either side, so that if this middle cut were re-run it would be possible to assign most of the products to one or other of its neighbours, resulting in the virtual extinction of the middle cut, and, as previously indicated, culminating in the separation of the charging stock into extreme low- and high-gravity components.

If Cuts 1 and 3 were also re-run, a further segregation would result. This has actually been achieved, and a partial reproduction of the results obtained suffices to indicate the significance of the effect under the given experimental conditions.

The upper allocation does not show all the fractions individually received (24), but is intended to reveal the spread obtained. The bulked primary fraction of sp. gr. 0·877 on re-running yields about 30 per cent. of a fraction of markedly lower specific gravity than the lowest gravity fraction, 0·857, received in the initial filtration, as compared with a corresponding fraction of 7 per cent. only from the second bulked fraction of sp. gr. 0·921.

This result does not appear unexpected, for the compounds for which the gel has least retentivity would be expected to show the poorest segregation, as is actually the case. It would be better either to re-run individual fractions or to expand the first column of gel. Nevertheless in spite of the admitted imperfect separation, the level achieved is in fact considerably in excess of the conventional, as will be shown subsequently.

Table III has already shown the yield and specific gravity of the bulked fractions. The further properties of the light cuts are given in Table VI.

TABLE VI.

*Low Gravity Compounds (Light Cuts) Derived from Fractions of Dewaxed Pressable Wax Distillate.*

| Charging stock. | | Per cent. by vol. of | | Sp. gr. at 60° F. | Visc. at 140° F. | Setting point, ° F. | Visc. gravity const. | Visc. index. |
|---|---|---|---|---|---|---|---|---|
| Sp. gr. at 60° F. | Visc. at 140° F. | Charge. | Dewaxed P.W.D. | | | | | |
| 0·868 | 34 | 67·7 | 13·4 | 0·820 | 33·5 | 28 | 0·803 | — |
| 0·895 | 39 | 61·2 | 12·1 | 0·834 | 36·2 | 50 | 0·805 | — |
| 0·920 | 53 | 54·9 | 11·9 | 0·845 | 43·2 | 14 | 0·806 | — |
| 0·938 | 125 | 51·7 | 9·8 | 0·865 | 66·3 | 30 | 0·809 | 106 |
| 0·956 | 519 | 47·2 | 10·1 | 0·874 | 125 | 36 | 0·806 | 106 |

The above are all white oils, characterized by an exceptionally low specific gravity for the boiling range they represent (cf. Table II), and are obtained in much higher yield than by batch solvent extraction using liquid $SO_2$ followed by phenol. Batch extraction is admittedly inefficient, and the following figures illustrate the comparative standing.

*Procedure A.*

Dewaxed P.W.D. 100%
| Distilled
21·8% Residue
| Silica gel, once through treatment
Low-gravity component, % by vol. of dewaxed P.W.D., 10·1

| | |
|---|---|
| Sp. gr. at 60° F. . . . | 0·874 |
| Visc., Redwood, 140° F.. | 125 |
| V.I. . . . . | 106 |
| V.G.C. . . . . | 0·806 |
| Setting point, ° F. . | 36 |

*Procedure B.*

Dewaxed P.W.D. 100%
| Treated 150% liquid $SO_2$ in countercurrent without backwash
Raffinate 64%
| Distilled under same conditions as in Procedure A.
Residue 6·4%
| 5 × 100% phenol at 60° C.
Low-gravity raffinate, % by vol. of dewaxed P.W.D., 3·0

| | |
|---|---|
| Sp. gr. at 60° F. . . . | 0·872 |
| Visc., Redwood, 140° F.. | 116 |
| V.I. . . . . | 107 |
| V.G.C. . . . . | 0·805 |
| Setting point, ° F. . | 38 |

The use of the adsorption procedure as compared with batch extraction trebles the yield, and hence gives an entirely different picture of the general chemical composition. It is freely admitted that the solvent extractions shown do not take advantage of the now prevailing conceptions for the effective execution of the operation. Nevertheless facilities for counter-current extraction using backwash and a temperature gradient do not exist in many laboratories, and also where a direct comparison has been effected, the separation secured by the single gel treatment using the quantities given has been found to compare very favourably with that secured by advanced solvent treatment.

The foregoing serves to exemplify the application of adsorption analysis to distillate stocks. In the analysis of residual stocks, long residues should be distilled to overhead cuts of restricted boiling range comparable with those of Table II, leaving a secondary distillation residue with an initial boiling point of about 300° C. at 10 mm. pressure. The latter will compare in boiling range to a normal residual bright stock, which under the conditions of a Peterkin 10-mm. distillation test show a 50 per cent. point of 340–350° C. uncorrected. Stocks of this boiling range need not be distilled further, but may be subjected to adsorption analysis as received. If wax bearing, they may advantageously be filtered without prior separation of the wax, permitting the whole of the wax to be recovered in a much purer condition than would be the case if dewaxing were the first step.

The processing of this type of residual stock may be illustrated by data secured from the treatment of a crude residue of sp. gr. 0·980 containing both wax and hard asphalt. This stock, from which 6·9 per cent. of hard asphalt was separated on making up the solution in petroleum ether, was filtered through gel at a ratio of 11·4 gm. of gel per gram of stock remaining after separation of asphaltenes. This ratio, nearly double the normal, was necessitated by the ease with which the dark-coloured soluble component was washed out of the gel. The quantitative record was as follows :—

TABLE VII.

*Treatment of Asphaltic Crude Residue of Sp. Gr. at 60° F., 0·980.*

| Fraction No. | Per cent. by weight. | | Fraction. Sp. gr. at 60° F. | Dewaxed oil. | | V.I. |
|---|---|---|---|---|---|---|
| | Fraction. | Dewaxed fraction. | | Sp. gr. at 60° F. | Visc. at 140° F. | |
| 1–7 | 35·94 | 30·99 | — | 0·880 | 481 | 100 |
| 8–11 | 7·71 | 7·03 | — | 0·915 | — | — |
| 12 | 3·19 | 3·19 | 0·938 | | | |
| 13 | 2·60 | 2·60 | 0·968 | | | |
| 14 | 4·42 | 4·42 | 0·991 | Fractions 1–11 dewaxed gave :— | | |
| 15 | 2·48 | 2·48 | 1·013 | Oil, sp. gr. at 60° F. | | 0·890 |
| 16 | 3·01 | 3·01 | 1·021 | Visc., Redwood, | | |
| 17 | 4·79 | 4·79 | 1·034 | 140° F. . . | | 571 |
| 18 | 6·96 | 6·96 | 1·047 | V.G.C. . . . | | 0·797 |
| 19 | 8·25 | 8·25 | 1·069 | V.I. . . . | | 93 |
| 20 | 13·80 | 13·80 | 1·091 | Setting point, ° F. . | | 32 |
| Asphaltenes | 6·85 | 6·85 | — | | | |
| Wax | — | 5·63 | — | | | |
| | 100·00 | 100·00 | | | | |

Whilst the foregoing procedure has the disadvantage of yielding a number of wax-bearing fractions which do not lend themselves to individual characterization, this is outweighed by the two-fold advantage of improved ease of dewaxing coupled with isolation of the wax in a relatively pure condition.

Having illustrated the use of the method herein termed "adsorption analysis," a development of the general operation known as chromatographic adsorption, points of interest emerging from the foregoing examples and other analyses are presented.

## The Variation of Crude Composition and Component Properties with Boiling Point.

The data already presented in Table IV show that there is a regular transition in composition for that particular crude. The content of low-gravity compounds diminishes with boiling point and is counterbalanced by an increased content of high-gravity compounds. As Cannon and Fenske (*loc. cit.*) have already noted, the low-gravity compounds display a much less marked transition in properties than do the high-gravity components. A comparison of properties is given in Table VIII.

Table VIII.

*Comparison of Cuts Derived from a Dewaxed Pressable Wax Distillate.*

| No. | Cut. | | Low-gravity component. | | | High-gravity component. | | Condition. |
|---|---|---|---|---|---|---|---|---|
| | Mid b. pt. at 10 mm., ° C. | Molar wt. | Sp. gr. at 60° F. | Molar wt. | Visc., Redwood, 140° F. | Sp. gr. at 60° F. | Molar wt. | |
| 1 | 157 | 240 | 0·820 | 265 | 33·5 | 1·008 | 207 | Mobile fluid. |
| 2 | 189·5 | 270 | 0·834 | 297 | 36·2 | 1·030 | 243 | ,, ,, |
| 3 | 220 | 310 | 0·845 | 365 | 43·2 | 1·037 | 265 | Oil. |
| 4 | 252 | 347 | 0·865 | 400 | 66·3 | 1·050 | 328 | Soft resin. |
| 5 | 294 | 408 | 0·874 | 460 | 125 | 1·058 | 386 | Hard resin. |

The molecular weights were determined by freezing-point depression. The molar weight of the resinous component is always less than that of the parent cut, whilst that of the low-gravity component is always higher. Whilst the viscosities of the high-gravity components have not been determined, the variation described from a mobile fluid to a hard resin, in spite of a limited overall increase in specific gravity 0·050, almost the same as for the low-gravity components 0·054, emphasizes the findings of Cannon and Fenske. This marked transition in properties is associated with a marked increase in molecular weight, but not such an increase as to lend any countenance to a supposition that the solid resins have been derived by a process of polymerization. In fact, the molecular weights show these resins to be an original component of the crude petroleum, and not to have been formed by a degradation process after its initial formation.

This being so, their persistence as low-molecular-weight compounds affords further support to the low-temperature history of petroleum, for these compounds under heat treatment do not undergo condensation without decomposition, but yield high percentages of coke, together with a limited proportion of liquid distillate.

Comparison of the molar weight specific gravity and 50 per cent. boiling point indicates an approximate adherence to the working rule that "the molecular weight for a given boiling point is approximately inversely proportional to the specific gravity" (Nelson, "Petroleum Refinery Engineering," 1st Edition, p. 114).

## The Components of Residual Stocks.

A crude residue following a pressable wax distillate, in addition to lubricating-oil constituents, contains wax and high-gravity components in variable amount. Sometimes the high-gravity components are asphaltenes mixed with resinous material, together present in such proportion that the crude residue is utilized as asphalt. Other crude residues contain substantial percentages of resinous material precipitable by propane, but containing little or no asphaltenes. Again, a residue as from Penna. or Hardstoft may contain but little resin and be composed almost wholly of lubricating constituents of high hydrogen content. Such crudes contain but a limited proportion of wax.

Commercial bright stocks are usually derived from a crude distillation residue, but are sometimes manufactured from a heavy wax distillate cut.

The preponderating constituents of such stocks are low-gravity compounds of high hydrogen content, and the properties of some bulked cuts derived from a range corresponding to fractions 1–5 of Table I are given in Table IX.

Table IX.

*Properties of Low-gravity Cuts ex Bright Stock of Various Origin.*

| Origin. | Sp. gr. at 60° F. | Visc., Redwood. | | | V.G.C. | V.I. | Setting point, ° F. | Molar wt. | Appearance. |
|---|---|---|---|---|---|---|---|---|---|
| | | 100° F. | 140° F. | 210° F. | | | | | |
| Penna, commercial grade | 0·866 | 892 | 306 | 88·9 | 0·777 | 113 | 22 | 680 | Pale green. |
| Western commercial grade | 0·878 | 1224 | 383 | 94·8 | 0·791 | 97 | 34 | 730 | „ „ |
| Burma crude residual stock | 0·866 | 640 | 220 | 68·0 | 0·783 | 106 | 26 | 690 | White. |
| Dhulian crude residual stock | 0·880 | 1600 | 481 | 114 | 0·786 | 100 | 32 | 725 | „ |
| Dhulian crude distillate stock | 0·875 | 406 | 145 | 54 | 0·795 | 97 | 32 | 490 | „ |

The irregular variations in physical characteristics are supposed to be due to constitutional influences, but since the data cover but a limited range of crudes, elaborate deduction is not attempted. Nevertheless, it may be noted that the high-wax-bearing crude of Burma yields a white residual oil of low gravity and viscosity, whilst the Dhulian crude of comparatively low wax content yields oils of relatively high specific gravity

and viscosity, and so on. In the case of Burma crude the source materials responsible for the high wax content of the parent crude, covering a range of melting points up to the highest, and therefore containing, it may be assumed, long-chain structures, may also be supposed to yield lubricating oils the properties of which will be largely determined by the presence of long chains.

In addition to these compounds of low specific gravity, bright stocks contain other components of lower hydrogen content, and higher specific gravity, which in the extreme are solid resins. Typical compositions are shown by the following analyses of commercial samples of Penna. and Western bright stocks.

TABLE X.

*Adsorption Analysis of Penna. and Western Bright Stocks.*

| Fraction No. | Filtrate, ml. | Per cent. by vol. | | Sp. gr. at 60° F. | |
|---|---|---|---|---|---|
| | | Fraction. | Cumulative. | Fraction. | Cumulative. |
| | Low-cold-test Penna. Bright Stock—Sp. gr., 0·891. Viscosity at 140° F., 595. | | | | |
| 1 | 100 | 16·9 | 16·9 | 0·863 | 0·863 |
| 2 | ,, | 12·6 | 29·5 | 0·867 | 0·865 |
| 3 | ,, | 13·3 | 42·8 | 0·867 | 0·865 |
| 4 | ,, | 14·2 | 57·0 | 0·867 | 0·865 |
| 5 | ,, | 15·5 | 72·5 | 0·876 | 0·867 |
| 6 | ,, | 4·5 | 77·0 | 0·902 | 0·870 |
| 7 | ,, | 3·1 | 80·1 | 0·909 | 0·871 |
| 8 | ,, | 2·3 | 82·4 | 0·915 | 0·873 |
| 9 | 200+ | 4·0 | 86·4 | 0·929 | 0·876 |
| 10 | M.E.K. extract | 5·2 | 91·6 | 0·945 | 0·880 |
| 11 | ,, | 3·5 | 95·1 | 0·971 | 0·884 |
| 12 | ,, | 4·9 | 100·0 | 1·001 | 0·889 |
| | High-viscosity Western Bright Stock—Sp. gr., 0·916. Viscosity at 140° F., 960. | | | | |
| 1 | 100 | 13·8 | — | 0·870 | 0·870 |
| 2 | ,, | 10·5 | 24·3 | 0·876 | 0·874 |
| 3 | ,, | 11·8 | 36·2 | 0·874 | 0·874 |
| 4 | ,, | 12·6 | 48·7 | 0·881 | 0·875 |
| 5 | ,, | 12·35 | 61·05 | 0·888 | 0·879 |
| 6 | ,, | 5·7 | 66·75 | 0·911 | 0·881 |
| 7 | ,, | 3·6 | 70·35 | 0·923 | 0·882 |
| 8 | ,, | 2·5 | 72·85 | 0·930 | 0·884 |
| 9 | 200+ | 4·9 | 77·75 | 0·943 | 0·888 |
| 10 | M.E.K. extract | 5·2 | 82·95 | 0·982 | 0·894 |
| 11 | ,, | 5·65 | 88·6 | 0·998 | 0·901 |
| 12 | ,, | 11·4 | 100·0 | 1·036 | 0·916 |

These conventional bright stocks are characterized, therefore, by a substantial content of compounds of minimum specific gravity, associated with a smaller content of compounds of intermediate specific gravity and high-gravity resins present in variable amount. The Penna. stock contains but a small percentage, if any, of genuine high-gravity resin, since the final 4·9 per cent. fraction has a gravity of no more than 1·001. However, Western Stock is richer in high-gravity compounds. The characteristic

fluorescence of the commercial grades is associated with the presence of these high-gravity compounds, but is not necessarily shared equally by all. Adsorption analyses on unrefined Eastern Stocks in which the used gel was divided into parts and extracted with a series of solvents of progressive solvent power, in the order aromatic free petroleum ether, naphtha and methyl ethyl ketone, revealed that the maximum fluorescence was associated with the portion recovered by the first-named solvent. Further, a solvent-refined stock still containing resin in limited amount, on treatment in naphtha solution with acid and clay—which operation undoubtedly removed discoloured high-gravity resin in substantial proportion—yielded a finished oil of intense green cast. This final cast is considered to have been obtained by a process of subtraction, and not of synthesis, the green fluorescence, or at any rate the major proportion thereof, being attributable to compounds of high specific gravity present in limited amount.

## Comment.

The foregoing serves to show that the adsorption technique is widely applicable to the study of heavy oils by the separation of components of widely different properties. It does not appear to cause polymerization of any major component to an appreciable degree, although it is conceivable that a cracked product would be so affected. In all examples explored, with the exception of Pennsylvania bright stock, the average molecular weight of the high-gravity components has been found to be less than that of the low-gravity component, and therefore the former have not been formed by a condensation of more saturated compounds of the type now existent in the various oils, either in nature or during the analysis. Catalytic oxidation by oxygen contained within the adsorbent represents a further possible disturbing influence. The potential significance of these hypothetical effects will vary with the object of the investigation. For the broad examination of a lubricating or wax-bearing stock either effect will be without real significance, but if it be wished to study a component suspected to be present in small amount, then catalytic phenomena may cause interference.

The use of adsorbents other than silica gel has been mentioned. In view of the degree of separation achieved by the preferred adsorbent, these have not been exhaustively explored, but bauxite and charcoal have been studied in some detail. Bauxite appears to separate high-molecular-weight residual stocks almost as well as does silica gel, but falls very far behind in the resolution of distillate stocks of the type characterized in Table II. Superfiltchar, Petrisil bleaching earth, etc., have also been employed, but the separations were out-distanced by silica gel.

It is clear that the experiments and results recorded herein do no more than to adumbrate the possibilities of the procedure. The results do not achieve the minute sub-division attaching to investigation on a larger scale, but the suggestion may be advanced that the present degree of resolution is comparable with the levels attained by more elaborate procedures and is withal attained at a reasonable expenditure of time and material.

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*Research Department,*
*Fairlawn,*
*Honor Oak Road,*
*Forest Hill, London, S.E. 23.*

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# SCIENCE, NATIONAL AND INTERNATIONAL, AND THE BASIS OF CO-OPERATION.*

By Dr. A. V. Hill, M.P.

I SHOULD be the last to claim that we scientific men, as a class, are less liable to prejudice on grounds of self-interest, race, politics, or religion than other educated people; and we should deceive ourselves, and perhaps some uncritical members of the public, if we were to assume (as some of us seem to do) that scientific eminence, or the scientific habit of mind, as such, or even scientific notoriety, give any special virtue to our opinions on more ordinary topics. It is, nevertheless, a fact that the nature of our occupation makes scientific men particularly international in their outlook. In its judgments on facts science claims to be independent of political opinion, of nationality, of material profit. It believes that Nature will give a single answer to any question properly framed, and that only one picture can ultimately be put together from the very complex jigsaw puzzle which the world presents. Individual and national bias, fashion, material advantage, a temporary emergency, may determine which part of the puzzle at any moment is subject to the greatest activity. For its final judgments, however, for its estimates of scientific validity, there is a single court of appeal in Nature itself, and nobody disputes its jurisdiction. Those who talk, for example, of Aryan and non-Aryan physics, or of proletarian and capitalist genetics, as though they were different, simply make themselves ridiculous. For such reasons the community of scientific people throughout the world is convinced of the necessity of international collaboration; has practised such collaboration for many years, indeed along the centuries; and has built up an elaborate system of congresses and unions of standards, units and nomenclature, and of abstracting journals, together with a widespread interchange of research workers and ideas from one country to another.

## International Co-operation in Science.

In no other form of human activity, therefore, has so complete an internationalism spread throughout the national structure of society: in no other profession or craft is there so general an understanding or appreciation of fellow-workers in other parts of the world. This implies no special merit or broadmindedness on the part of scientific men; it is their very good fortune, a good fortune which involves obligations as well as privileges. For example, when the Nazis in 1933 began their persecution of Jews and liberals in Germany, it was the scientific community in many other countries which came most quickly to the rescue of their colleagues: not out of any special generosity but because *firstly* they had personal knowledge of those

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who were being persecuted, and *secondly* they realized that such persecution struck at the basis of the position of science and scientific workers in society. Again in the treatment of aliens in this country during the present war, the scientific community more than any other, and quite regardless of political complexion, has stood for a liberal and reasonable policy: desiring both to maintain the high tradition which the world of learning has inherited from the past, and also to make use of the willing help of people whom it knew personally to be loyal to the cause of freedom for which we are fighting. Again, in the United States to-day there is no section of the public so unanimously concerned for the victory of British arms as the community of university and particularly of scientific people. These realize that the basis of all progress in science and learning is international co-operation, and they cannot conceive how such co-operation could be possible under a Nazi domination of the world.

It may well be, then, that through this by-product of international co-operation science may do as great a service to society (just as learning did in the Middle Ages) as by any direct results in improving knowledge and controlling natural forces: not—as I would emphasize again—from any special virtue which we scientists have, but because in science world society can see a model of international co-operation carried on *not merely for idealistic reasons, but because it is the obvious and necessary basis of any system that is to work.*

One of the great tasks lying before scientific people after the present war will be to rebuild, and to rebuild on a firmer and better foundation, the international scientific organizations which have come into being in the last seventy years, particularly during the present century. The earliest of these was the International Bureau of Weights and Measures, established in 1873. An International Geodetic Association followed, and in 1903 an International Seismological Association on the same lines. Arising from the initiative in 1898 of the Academies of Munich and Vienna, together with the Royal Societies of Göttingen and Leipzig, which had all been in the habit of meeting annually, the Royal Society (of London) undertook to approach a number of foreign academies with a view to the formation of an international association of academies. As an independent institution, not subject to State control as were so many of the academies, the Royal Society was in a very favourable position for opening such negotiations. As a result the International Association of Academies was formed, which held five meetings in all, the sixth at St. Petersburg being cancelled owing to the outbreak of war in 1914. It never met again.

These meetings were not limited to natural science, many of the academies being concerned both with the scientific and the humanistic side of learning. It is interesting that as one result of this movement, and in order to represent Great Britain on the literary, philosophical, and historical sides, the British Academy was formed and incorporated by Royal Charter in 1902. We of the Royal Society have always hoped that the British Academy will ultimately take the same place in national life in respect of humanistic studies, as the Royal Society has long had in respect of "natural know-

ledge." There is need for such independent bodies of high standing and disinterested outlook, particularly when so many functions are being taken over, often quite suddenly and without anyone noticing, by the State. The Royal Society, in spite of its independence, has always, since its foundation in 1662, had close relations with the Government, and it would take a small book to recount the many occasions on which its advice has been asked. It has recently been given still another privilege and duty, under the Lord President, in advising the War Cabinet on scientific matters through its President and Secretaries, who are members of the Scientific Advisory Committee. One hopes that, in some form or other, this function, no less necessary in peace-time, will continue after the war. *Could not a similar provision be usefully made now for those complementary studies which the British Academy represents?* This is an interpolation, not strictly relevant to the thesis of this address, but I feel it is of some importance. The reconstruction of Britain and of our international relationships, in learning and the arts of peace, as well as in social and economic directions, is a matter of great concern about which we should be thinking already. In so doing, a disinterested body of such high standing as the British Academy, with no particular political axe to grind, might render the greatest possible service to the State. Science will have a special part to play, now and in the future, in national and international affairs, and it is right that independent science should have access to the chief centre of government. Other branches, however, of disinterested learning, have an equal if different application, and one would like to see for them a similar machinery created. Science is at last coming into its own in relation to social, national, and international affairs. The older branches of learning, too long contemptuous, have begun to realize the situation: but that need not mean that social, historical, economic, literary, and philosophical studies will have their influence diminished; only that the influence of learning as a whole will be increased.

To return to my story; just before the end of the last war, in 1918, representatives of the academies of all the allied countries met in London, and later in Paris, to discuss the formation of a new international scientific organization. In July 1919, the first General Assembly of the International Research Council, as it was to be called, met in Brussels. Representatives of the Central Powers were not invited, and a misunderstanding which then arose was made an excuse for declining an invitation which was sent to each of them a few years later. This unfortunate state of affairs persisted. German professors who feel themselves insulted are difficult people to appease, and indeed the fault was not all on their side. International Unions for Astronomy, Geodesy and Geophysics, Chemistry and Mathematics (this last no longer in existence) were formed; and at the next General Assembly in 1922, for Physics, Scientific Radio, Geography, and Biology. Some of these Unions have functioned well and have held important international congresses and done important work; others have done little. The ones that have worked best, *e.g.*, Scientific Radio, are those which had a more practical international task to fulfil.

These Unions always had an official or semi-official flavour: official delegates, official hospitality, official finance, official business, have tended

to put independent science into a somewhat subordinate position. Physiologists have held International Congresses for fifty years, and great value these have had, as we know who have taken part in them: but physiologists have always insisted that they came as independent scientists, to meet, to hear and to discuss things with their colleagues; not as representatives of some State institution or interest. Other scientific groups have held similar informal congresses based on the same idea. There is grave danger, as was found by the Physiological Congress meeting in Italy in 1932, and in the Soviet Union in 1935, of a congress being used as an opportunity for political propaganda: in 1938 this was altogether avoided by the tact and understanding of Swiss colleagues, as it had been avoided at meetings prior to 1932. Political considerations are hard enough to avoid anyhow, but they are much worse if a congress is not genuinely independent.

In this country and in America, the great strength and the high position of the independent scientific societies make it easy for them to take charge of the proceedings of a congress, or of an enquiry of international importance, without danger of State control—either in appearance or reality. But this is not so easy, indeed it has been impossible in recent years, in many countries. In order to preserve the integrity of science in our own country, it is very important that those strong independent scientific bodies should be maintained: and for the sake of international scientific relations it is desirable that in other countries also, so far as we can influence them, the domination of the State over science should be tempered by public appreciation of the part played by independent scientific agencies and institutions.

In some form or other, not one may hope exactly in their present form, these International Unions must be started up again some day. This time, at any rate, we shall not be prevented from following our better judgment by the intransigence of French colleagues: though it may be hard enough for us this time to take a detached view. My own feeling is that in this matter we should rely, as far as possible, upon the help and advice of our American scientific friends. Their views about science, for its own sake and in relation to the State, are much the same as ours, and they (at present at least) are further from the battle. I know they would regard it as a sacred trust of friendship to bear a large part of the burden of starting off again the international co-operation in scientific endeavour which was so unhappily ended by the events of the last years.

In America, as in Britain, science is largely independent of the State. There, as here, great scientific organizations work under Government auspices: there, far more than here, the great corporations maintain their research departments: there, as here, free universities and free endowments are engaged in promoting the advance of scientific knowledge: there, as here, free and independent science is able to co-operate with the scientific agencies of government and industry, to the great advantage of all. There is a high idealism in America about international co-operation in the field of science and learning, and a very great regard for British science and British scientists. If the war goes ultimately as we expect,

in the downfall of dictatorship and tyranny, it will be our job to start off again, on broader and better lines, the complex system of international scientific co-operation: and in starting it off I am sure that we shall be able to call for the help and co-operation, without stint or limit, of our scientific friends in America.

## Desiderata in State Research.

I have spoken several times of the necessity of guarding the independence, the spiritual integrity of science. In many countries to-day science is wholly subservient to the State: its soul is not its own. I do not deny for a moment the importance, indeed the necessity, of scientific organizations within the framework of government, or of liberal support by the State of scientific research. One can only welcome such recognition by the public of the importance of scientific knowledge and scientific discovery—and ask for more. There are several things, however, which one may fear. *Firstly*, the condition of stagnation and complacency which tends to develop in any scientific department or establishment which is cut off from outside criticism or ideas: we have far too many examples of this already, formidable examples, and if we are not careful they will multiply; the reduction of science to official routine can be a real menace. *Secondly*, the danger that science will be planned by administrators in offices instead of by young men with their sleeves rolled up, in laboratories or workshops. *Thirdly*, the disadvantage of separating teaching from research, to the great loss of the next generation who may miss the inspiration of seeing discovery going on in the places where they are taught. *Fourthly*, a decrease in the influence and prestige of those independent scientific bodies which play so large a part in the social and intellectual activities of the scientific community and provide the cross-connections between groups which might otherwise be isolated. *Fifthly*, the danger that he who pays the piper may call the tune, and that research may be required to be devoted primarily to objects which the politician, or the civil servant, regard for the moment as of national importance; or even—as in Germany and the Soviet Union—to bolstering up theories which the official philosophy of the State prescribes.

To avoid all these troubles, the independence and integrity of science must be carefully preserved; in the universities, in the learned societies, in the various associations or institutions devoted to the advancement of knowledge. Whenever State support is given, a buffer should be interposed, similar to that provided by the University Grants Committee between the universities and the Treasury. In our existing Research Councils (Department of Scientific and Industrial Research, Medical Research Council, and Agricultural Research Council), working with Government funds, the buffer is already provided by the fact that the members of the Councils are chiefly independent scientific men. The same safeguard exists at present with much of our State-aided research: we must carefully watch that the strength of this safeguard is fully maintained, that it does not become a formality, and that the principle is consciously

extended wherever possible as the financial burden of scientific research and development is taken over (as is bound to happen more and more) by the State.

In many of the Departments of Government, however, notably those of the Defence Services, scientific research is undertaken on a grand scale, which cannot be controlled directly by outside independent bodies. In these establishments particularly, the danger of stagnation and complacency exists. They are devoted to specific service purposes, often of necessity secret: and the condition of secrecy prevents them, in ordinary times, from attracting many of the ablest and brightest minds, who prefer the freer atmosphere of the universities, the possibility of discussing and publishing their results, and the recognition of their colleagues resulting therefrom. Consequently in war those who direct these establishments are often people who have arrived at their positions by seniority and long service, during which they have been largely isolated from the ideas and criticism of current scientific thought: it has been difficult for them not to become officials rather than working scientists. When an emergency occurs, as at present, numbers of able men come in, but to posts in which they can exert relatively little influence, and their ability and imagination may for long be imperfectly used. This, indeed, is inevitable under the present system, for they have at first no experience of service conditions and needs. After a year or two perhaps, longer than necessary, these able people find their proper level, but not until much damage has been done by lack of imagination and energy in the posts they might have filled before.

To avoid this trouble—and it is a very real one—two main principles may be applied. *Firstly*, to introduce into each department or organization some kind of scientific advisory council, similar to that which on the whole works so well now in the Ministry of Supply. This council should consist partly of independent scientific men chosen for their special knowledge on the one hand, for their wide contact with the scientific community on the other: and partly of official scientific people representing not only the department or organization itself, but a variety of other departments, so that a good cross-section of official knowledge and experience is available. And *secondly*, in ordinary times to arrange for regular interchange of personnel between the Government research establishments and organizations, and the universities and other independent institutions in which research is carried on.

I know that this second proposal will shock some of those who have lived in the traditional secrecy of service science: but it is right all the same. Why should not a chemist or mathematician from Woolwich, a physicist from Signal School, an engineer from the Royal Aircraft Establishment, go back as a lecturer or professor to a university, or to the research staff in a commercial laboratory; just as a physiologist from the National Institution for Medical Research, or an aeronautical engineer at the National Physical Laboratory, or a zoologist at the Marine Biological Laboratory at Plymouth may do? And why should not the research workers in Government laboratories be just as regular attendants at the

meetings of scientific societies as those in other institutions? I sometimes thought, before the war, how good it would be to take a mission, harmonium and all, to one of the most important—and the most dead-alive—of these places and try to stir up a little general scientific enthusiasm.

It is difficult to get over vested interest and tradition in these things. As regards the first desideratum, that of an independent scientific advisory council within the framework of a Government organization, from a department where it does not exist already we are apt to get the reply from the political head or the permanent secretary, "When we want scientific advice we can always go to Sir X. Y.", not realizing that Sir X has sat in an office for years and that anyhow he cannot be knowledgeable on everything. Or we are told that the department has an excellent scientific organization of its own, which has in fact gone on without any expert criticism for many years, saved indeed from criticism by its well-preserved secrecy. Or it is said, "When we want scientific help we can turn to the D.S.I.R., the M.R.C. or the A.R.C., as the case may be." Those excellent bodies can in fact do much, but they cannot do more for other departments than answer specific questions. A large part of scientific work lies in formulating the questions to be asked, and that cannot be done except by people who are in close personal touch with the actual needs. A family doctor, in fact, is wanted, to watch over the scientific health of the department: to call in a consultant alone at intervals is little use: the family doctor must be available to realize the need and to understand the situation of the patient—*then* the consultant's advice is valuable. The three research councils are to be regarded as consultants, excellent and essential ones; but they do not make it unnecessary to have independent advice within a department.

As regards the second desideratum—that of a free interchange of personnel, backwards and forwards between Government establishments and the universities and other outside scientific institutions—the first need is for a common pension scheme. All scientific workers, whether in the universities, or in commercial laboratories, or in Government employment, should come under the Federated Superannuation System for Universities (F.S.S.U.), as do those employed by the three Research Councils (D.S.I.R., M.R.C., A.R.C.). Then the departments should insist on sending their people away at intervals, to carry on research elsewhere and to refresh their souls in institutions outside. Conversely, the departments should invite outside scientists (naturally under proper safeguards of secrecy when necessary) to work for corresponding periods in their establishments. The advantage of this second step would be that the importance and interest of the problems which are being tackled in Government establishments would be more commonly realized, and better men would be inclined to take part in their solution. In the defence services a reserve of officers and other ranks is an essential part of an efficient organization for war: in the scientific services, similarly, a reserve of research workers, for the case of emergency of any kind, would seem to be equally essential. I am not thinking only of war: other emergencies occur requiring the sudden application of scientific knowledge and method. It would be simple and

not very expensive to build up such a reserve of scientific talent, available for service when needed, and in so doing to introduce a new spirit and a new outlook into Government scientific establishments.

One great advantage of working in the scientific establishments, either of the Government or of a large company or corporation, is the fact that equipment is not limited below the minimum that is necessary for efficiency. In most of the free institutions, money for research is notoriously short. One of the great needs of research is better financial support, and in the relative poverty of charitable people and bodies to which I fear we must look forward for some time, this support will have to come from the State. One hears proposals made, for example, for a national research council to be set up to administer grants for research. In considering such proposals we should be wise to remember three principles:—

(*a*) That a powerful buffer is required to prevent the State from interfering with the integrity and independence of research, and to save research from being over planned and directed by officials sitting in Government offices;

(*b*) That it is often better to ask existing and experienced agencies, which we know to work, to undertake new jobs, in spite perhaps of apparent imperfections in their organization, rather than to allow our young revolutionaries to scrap the old and set up new schemes, cleaner on paper but untried;

(*c*) That the chief value of research grants will often be to young and comparatively unknown people, so that as far as possible devolution of allocation should be adopted, and the responsibility left to the university or other institution in which they work and where they are known.

I have tried to cover a large field in a very short time, and have been forced to deal for the most part with principles rather than details. I have omitted all reference to the pay and status of scientific people: the people themselves and the conditions vary widely, and for some men too much security, just as well as too little, may diminish their usefulness and initiative. I have not referred to the question of grants for students training for research, or of provision for weeding out those who show no scientific capacity: nor have I even mentioned scientific education, which would require a lecture to itself. And, lastly, I have not ventured to discuss how the scientific resources of the nation at war could be better utilized. That might involve, not only the usual items of criticism and the usual items of defence which we have all heard, but also—if properly undertaken—an exposure of facts which must at present be kept secret and of difficulties due to the personal peculiarities of individuals. Unfortunately when science comes, as it must come in war, into direct touch with action, it finds itself thwarted by intrigue, upset by unscrupulous exploitation of social and political connections, surrounded by personal ambitions and jealousies. These provide no small part of the difficulty in the way of utilizing our great scientific resources to the full. Blessed are they who remain innocently in their laboratories and grumble: for it is a thankless task to try to get things right.

One last word. In recent years a number of brilliant revolutionaries, filled with political zeal but without experience of affairs, have won great fame and applause by showing how Science is going to change the face of Society. The public is inclined to place these gentlemen on the same intellectual pedestal as Einstein, supposing that their science is as great as their chatter. The more responsible members of the scientific community are a little frightened by these activities—not because they grudge their colleagues their easy fame, but because the impression is put about that scientists as a whole claim to be allowed to dominate policy: and so, resistance is aroused to their more modest suggestion that they ought to be consulted. If these remarks should reach the ears of those on whom the task of formulating public policy falls, they can be reassured: The majority of scientific men are quite reasonable and have no grandiose ideas. We know our own limitations—as we are well aware of yours. All we ask is that we should be considered as equals in a common task—not merely as superior technicians paid to dish up the magic which you order.

# OLLETT TUBE CLEANER.

## A NOTE

By E. A. Evans.

The removal of carbon residue from Ramsbottom Coke bulbs is so laborious by chemical means, even with chromic acid, as to make it unattractive. War time shortages, however, have introduced the necessity for cleaning such tubes.

The simple expedient of burning off the carbon in oxygen presented itself. The apparatus shown (see opposite) indicates what a simple operation it can become. The bulb is placed on two supporting rods which can be rotated by a knurled knob. Oxygen is led into the bulb very gently through a platinum capillary. The bulb is carefully heated and rotated until the carbon disappears.

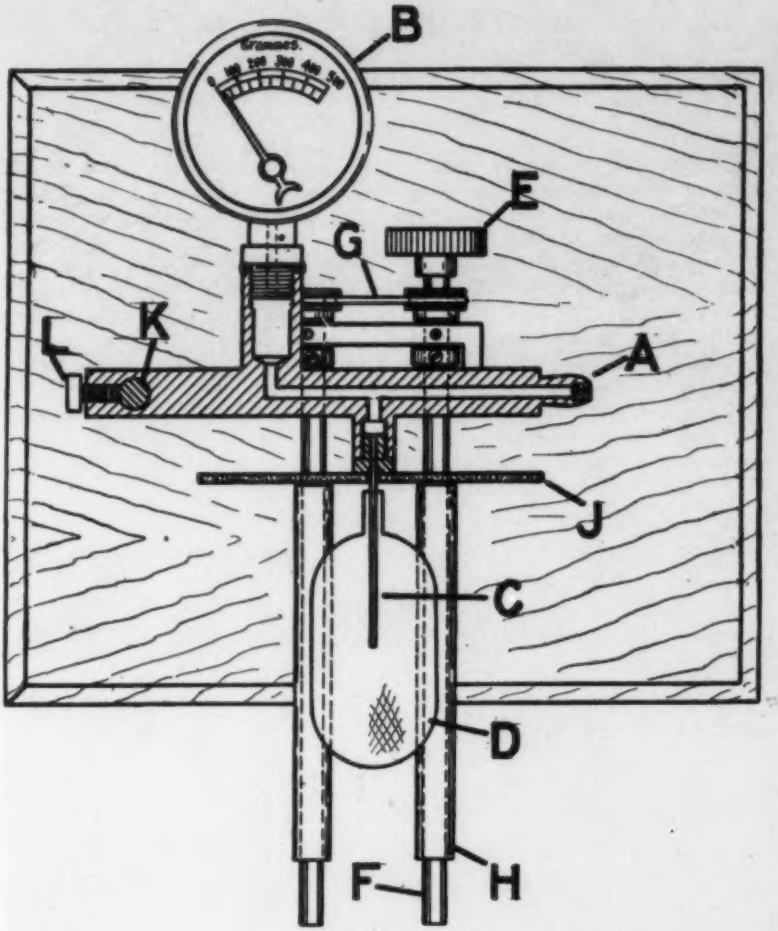
A few words of warning should be noted. Gentle heating only is necessary. Any excess heat tends to soften the glass and cause distortion. Too much oxygen with excessive heat will result in very high local temperatures, followed by bubbles being blown which finally burst.

Any residue which may remain from a pure oil is so small as to be negligible.

The time taken to clean a Ramsbottom coke bulb is anything up to four minutes.

This apparatus is easily adapted for the cleaning of other forms of apparatus contaminated with solid organic matter which is not explosive with oxygen.

The Author's thanks are due to C. C. Wakefield & Co., Ltd., for permission to publish this design.




OLLETT TUBE CLEANER

A. Oxygen Inlet.
B. Gauge.
C. Platinum Tube.
D. Ramsbottom Coke Bulb.
E. Rotating Knob.
F. Steel Rods.
G. Belt.
H. Silica Tubes.
J. Asbestos Shield.
K. Stand Rod.
L. Adjusting Screw.

B
A
C
D
H